

Supplementary Data

Magnetic MCM-41 nanoparticles as support for the immobilization of organometallic catalyst of palladium and its application in C-C coupling reactions

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Abstract:

In this work, surface of magnetic MCM-41 nanoparticles (MCM-41/Fe₃O₄) modified by 3-aminopropyltriethoxysilane (APTES) and further 1-methyl imidazole was anchored on its surface using cyanuric chloride as linker. Then, palladium nanoparticles were immobilized on the surface of modified MCM-41/Fe₃O₄ (Pd-imi-CC@MCM-41/Fe₃O₄) and further its application was studied as magnetically recyclable nanocatalyst in carbon-carbon coupling reactions between wide range of aryl halides and butyl acrylate, methyl acrylate, acrylonitrile, phenylboronic acid, or 3,4-difluorophenylboronic acid under phosphine-free ligand and air atmosphere. This catalyst has advantages of both Fe₃O₄ nanoparticles and mesoporous MCM-41. Catalyst structure was characterized using SEM, EDS, WDX, N₂ adsorption-desorption isotherms, XRD, TGA, FT-IR, and AAS techniques. All products from carbon-carbon coupling reaction were obtained with excellent yields and high TON and TOF values, which were indicate the high efficiency and activity of this catalyst. Heterogeneity and stability of Pd-imi-CC@MCM-41/Fe₃O₄ was studied by AAS technique, leaching test and poisoning test.

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Experimental details

Preparation of the catalyst

In the first step, amino-functionalized magnetic MCM-41 nanoparticles ($n\text{Pr-NH}_2@\text{MCM-41/Fe}_3\text{O}_4$) prepared according to new reported procedure [44]. In the next step, 1 g of $n\text{Pr-NH}_2@\text{MCM-41/Fe}_3\text{O}_4$ was dispersed in toluene and mixed with 2.5 mmol of cyanuric chloride (CC). Then, this mixture was stirred under reflux conditions for 24 h. The resulting solid ($\text{CC}@\text{MCM-41/Fe}_3\text{O}_4$) was separated using assistance of external magnet, washed with ethanol and dried at room temperature. Then, $\text{CC}@\text{MCM-41/Fe}_3\text{O}_4$ (1g) was dispersed in 50 mL toluene by sonication for 20 min, and 1-methylimidazole (5 mmol) was added to the reaction mixture. The reaction mixture was stirred under reflux conditions for 24 h under N_2 atmosphere. The resulting nanoparticles ($\text{imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$) were washed with ethanol for several times and separated *via* magnetic decantation and dried at 50 °C. In the final step, 0.5 g of $\text{imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$ and 0.25 g of palladium acetate were dispersed in DMSO for 20 min and stirred under N_2 atmosphere at room temperature for 3 h and was allowed to continue for 12 h at 60 °C. The reaction mixture was allowed to continue for 4 h at 100 °C. The final product ($\text{Pd-imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$) was separated by magnetic decantation and washed by ethanol and water to remove the unattached substrates and dried at room temperature.

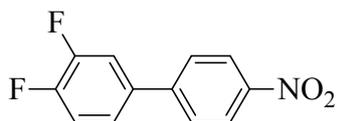
General procedure for Suzuki reaction catalyzed by Pd-imi-CC@MCM-41/Fe₃O₄

A mixture of aryl halide (1 mmol), 1 mmol of phenylboronic acid (PhB(OH)_2) or 3,4-difluoro phenylboronic acid (3,4-diF- PhB(OH)_2), Na_2CO_3 (3 mmol, 0.318 g), and $\text{Pd-imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$ (0.008 g, 1.5 mol%) was stirred in PEG-400 (1 mL) at 80 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down, $\text{Pd-imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$ was separated using an external magnet and washed with ethyl acetate. The remaining reaction mixture was extracted with H_2O and ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). Then ethyl acetate was evaporated and pure biphenyl derivatives were obtained in 85 to 98% of yields.

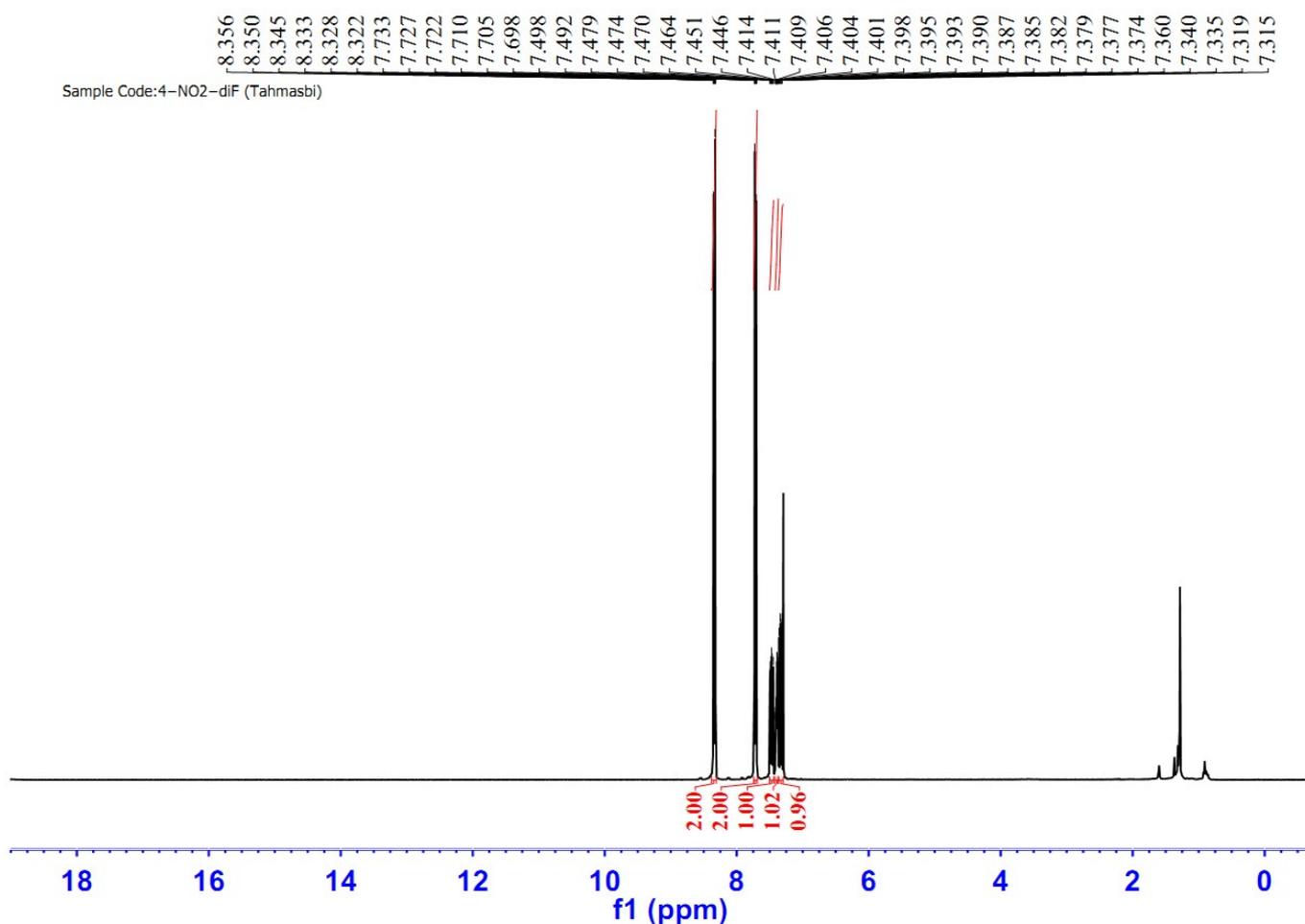
General procedure for Heck reaction catalyzed by Pd-imi-CC@MCM-41/Fe₃O₄

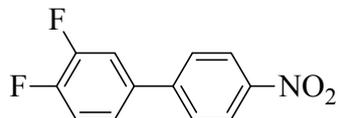
A mixture of aryl halide (1 mmol), 1.2 mmol of alkene (butyl acrylate, methyl acrylate or acrylonitrile), Na_2CO_3 (3 mmol, 0.318 g), and $\text{Pd-imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$ (0.012 g, 2.27 mol%) was stirred in PEG-400 (1 mL) at 120 °C and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled down to room temperature, $\text{Pd-imi-CC}@\text{MCM-41/Fe}_3\text{O}_4$ was separated using an external magnet and washed with diethyl ether. Then, the reaction mixture was extracted with H_2O and diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 (1.5 g). The diethyl ether was evaporated and pure products were obtained in 88 to 98% of yields.

¹H NMR spectral data

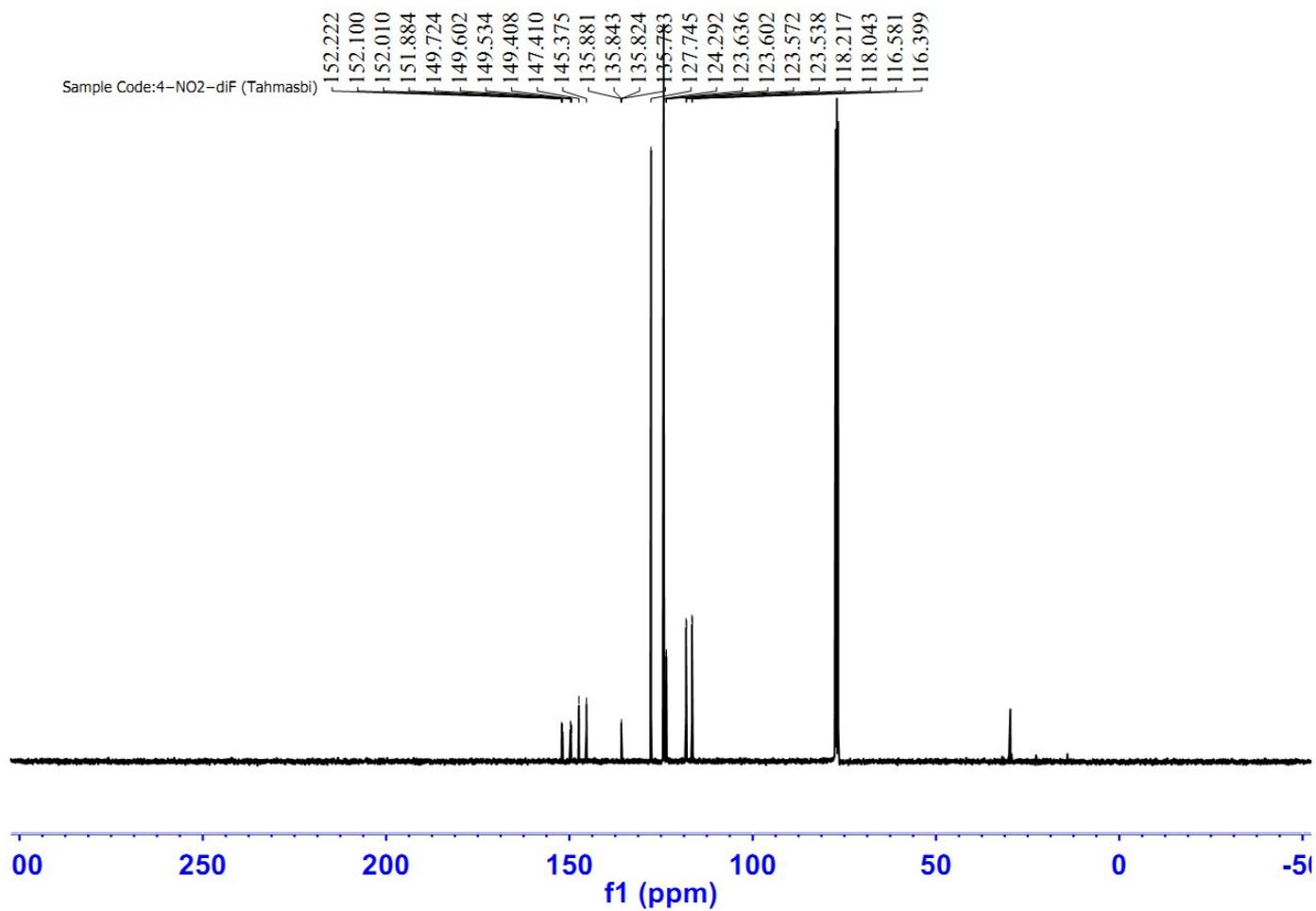


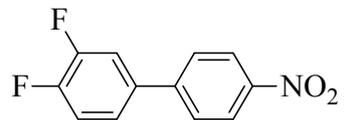
3,4-Difluoro-4'-nitro-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃): δ_H= 8.36-8.32 (dt, *J*= 8.8 Hz, *J*= 2 Hz, 2H), 7.73-7.70 (dt, *J*= 8.8 Hz, *J*= 2 Hz, 2H), 7.50-7.45 (m, 1H), 7.41-7.37 (m, 1H), 7.36-7.31 (m, 1H), ppm.



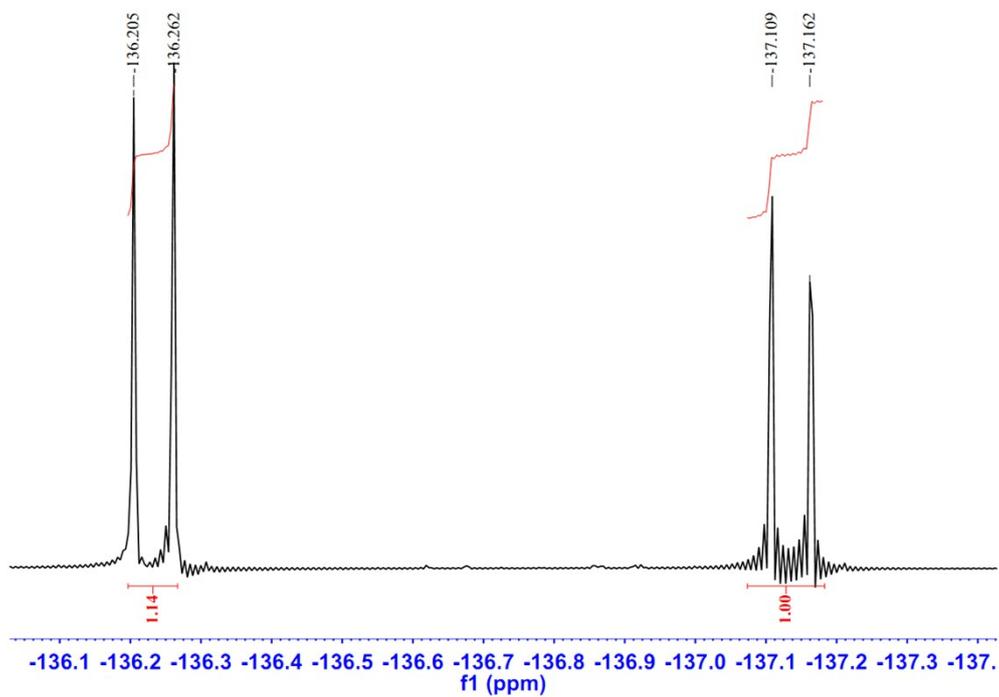
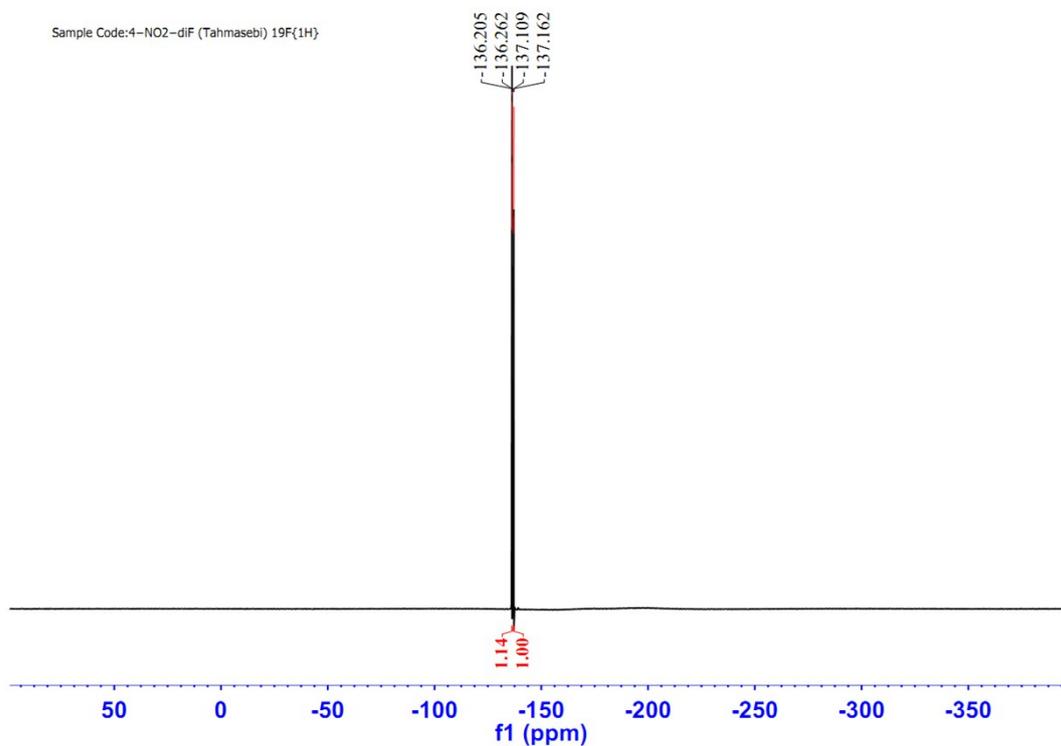


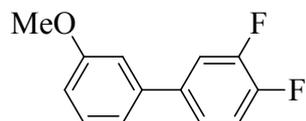
3,4-Difluoro-4'-nitro-1,1'-biphenyl: ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{H}} = 152.2, 152.1, 152.0, 151.9, 149.7, 149.6, 149.5, 149.4, 147.4, 145.4, 135.9, 135.84, 135.82, 135.7, 127.7, 124.3, 123.63, 123.60, 123.57, 123.54, 118.2, 118.0, 116.6, 116.4$ ppm.



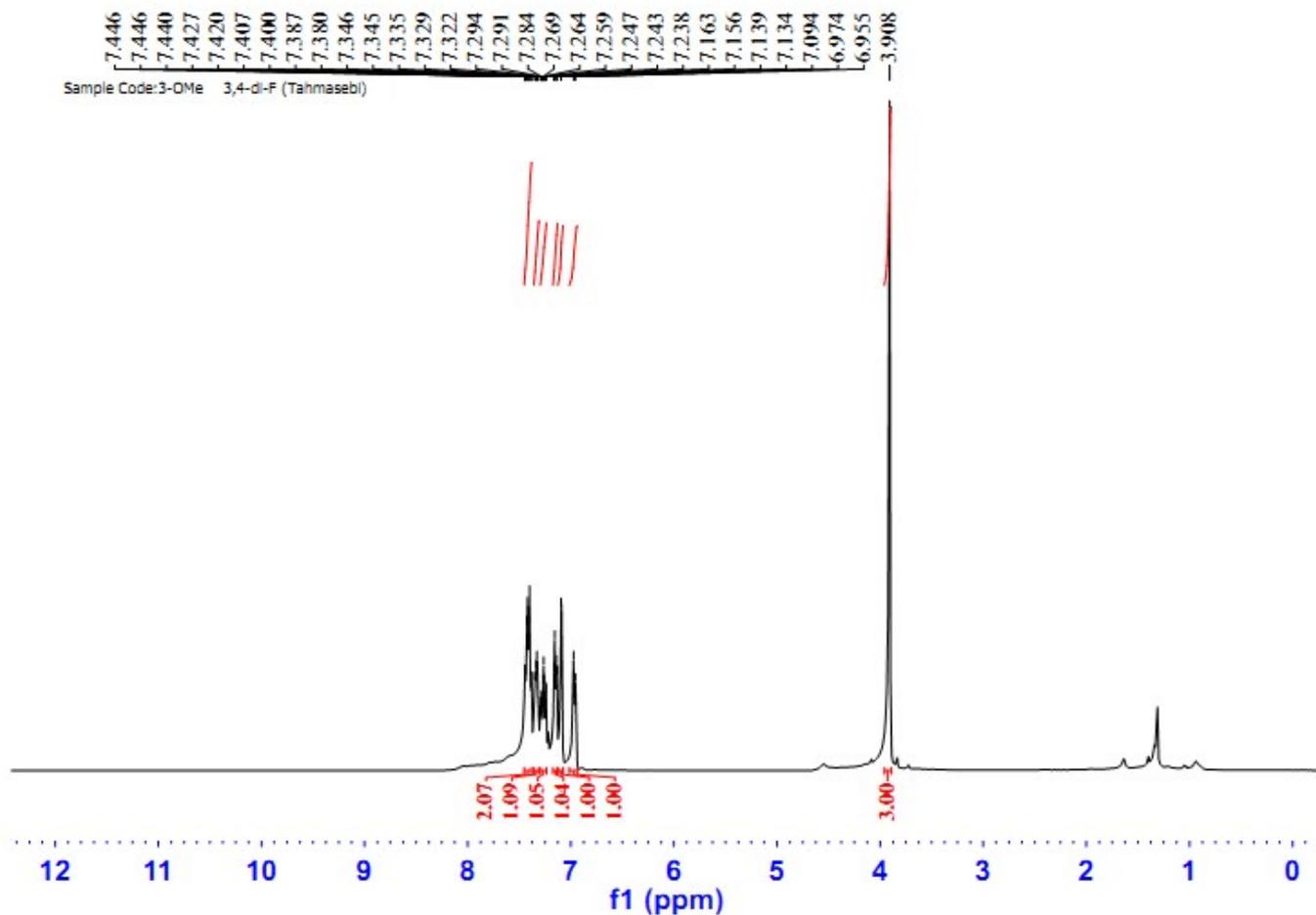


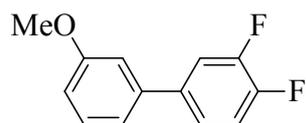
3,4-Difluoro-4'-nitro-1,1'-biphenyl: ^{19}F NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = -136.2$ (d, 1F), -137.1 (d, 1F) ppm.



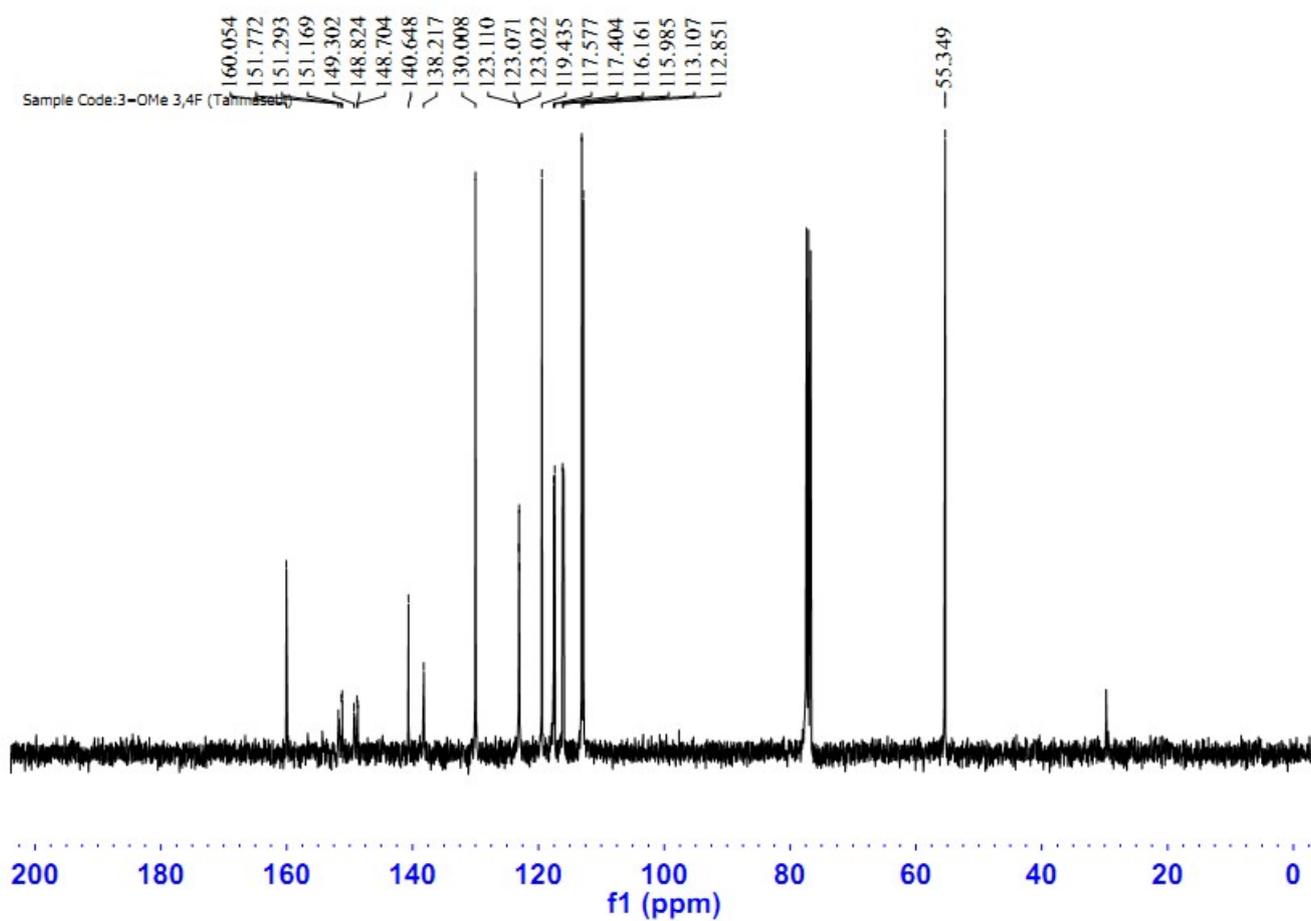


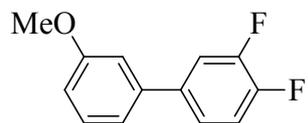
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.44\text{--}7.38$ (dd, $J = 8$ Hz, $J = 4$ Hz, 2H), $7.35\text{--}7.32$ (m, 1H), $7.29\text{--}7.24$ (m, 1H), $7.16\text{--}7.13$ (d, $J = 12$ Hz, 1H), 7.10 (s, 1H), $6.97\text{--}6.95$ (d, $J = 8$ Hz, 1H), 3.91 (s, 3H) ppm.



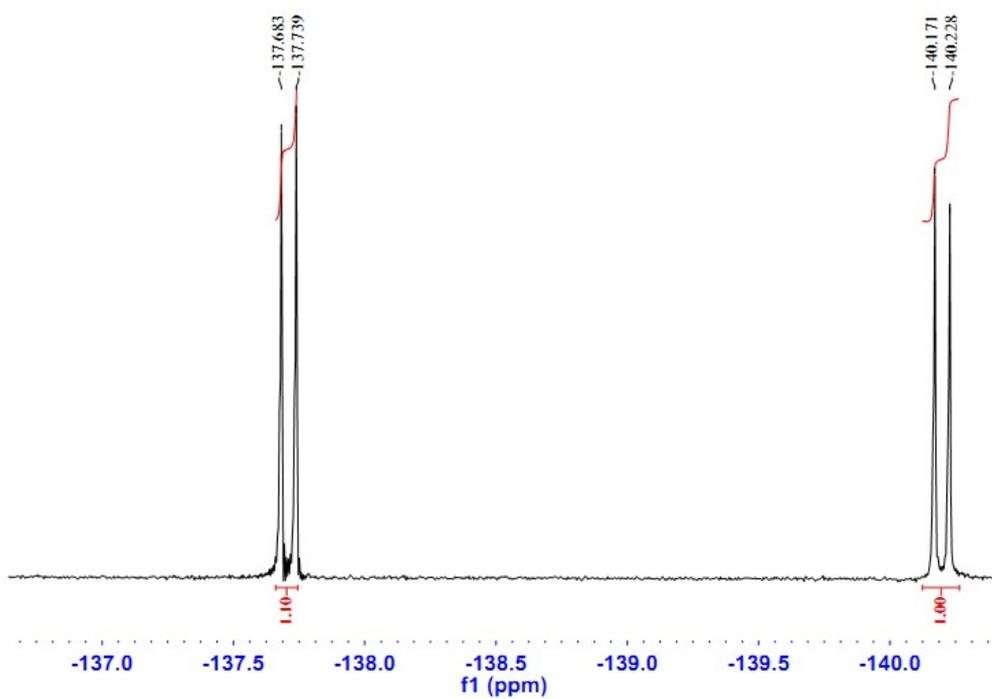
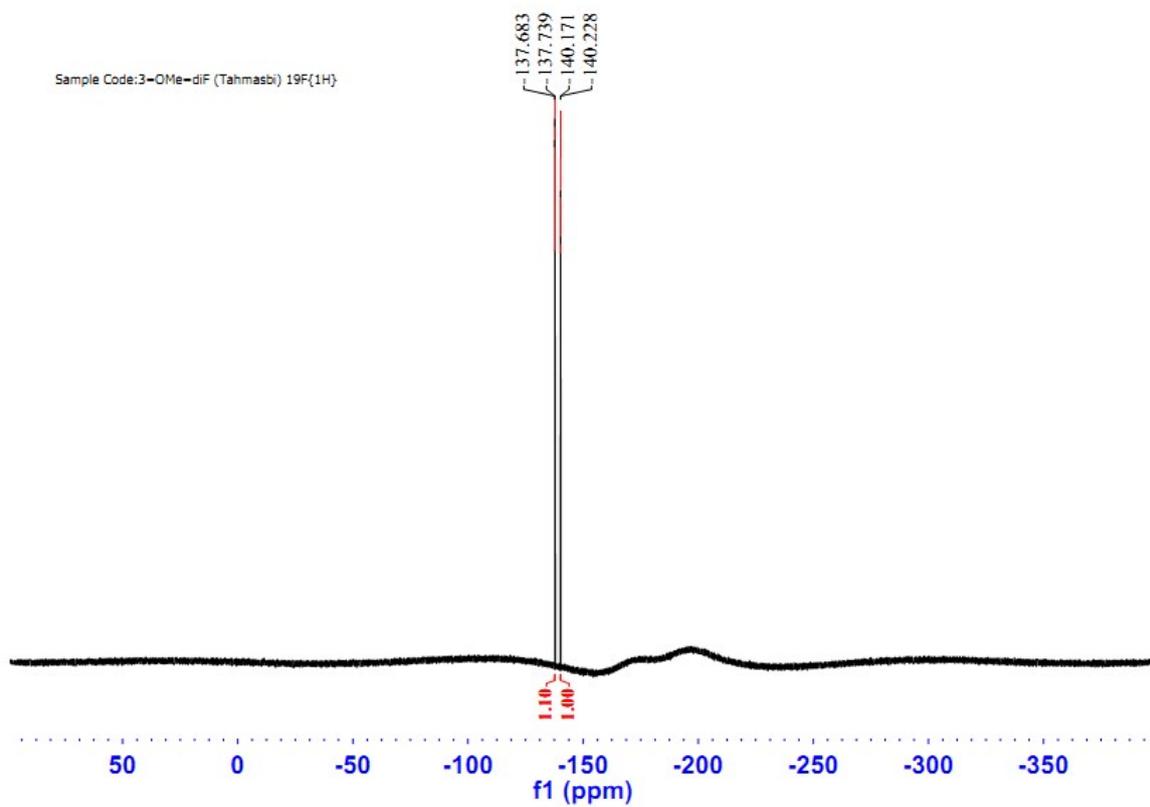


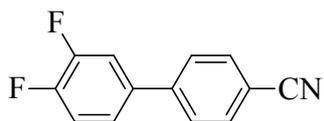
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: ^{13}C NMR (100 MHz, CDCl_3): δ = 160.0, 151.8, 151.3, 151.2, 149.3, 148.8, 148.7, 140.6, 138.2, 130.0, 123.1, 123.0, 119.4, 117.6, 117.4, 116.2, 116.0, 113.1, 112.8, 55.3 ppm.



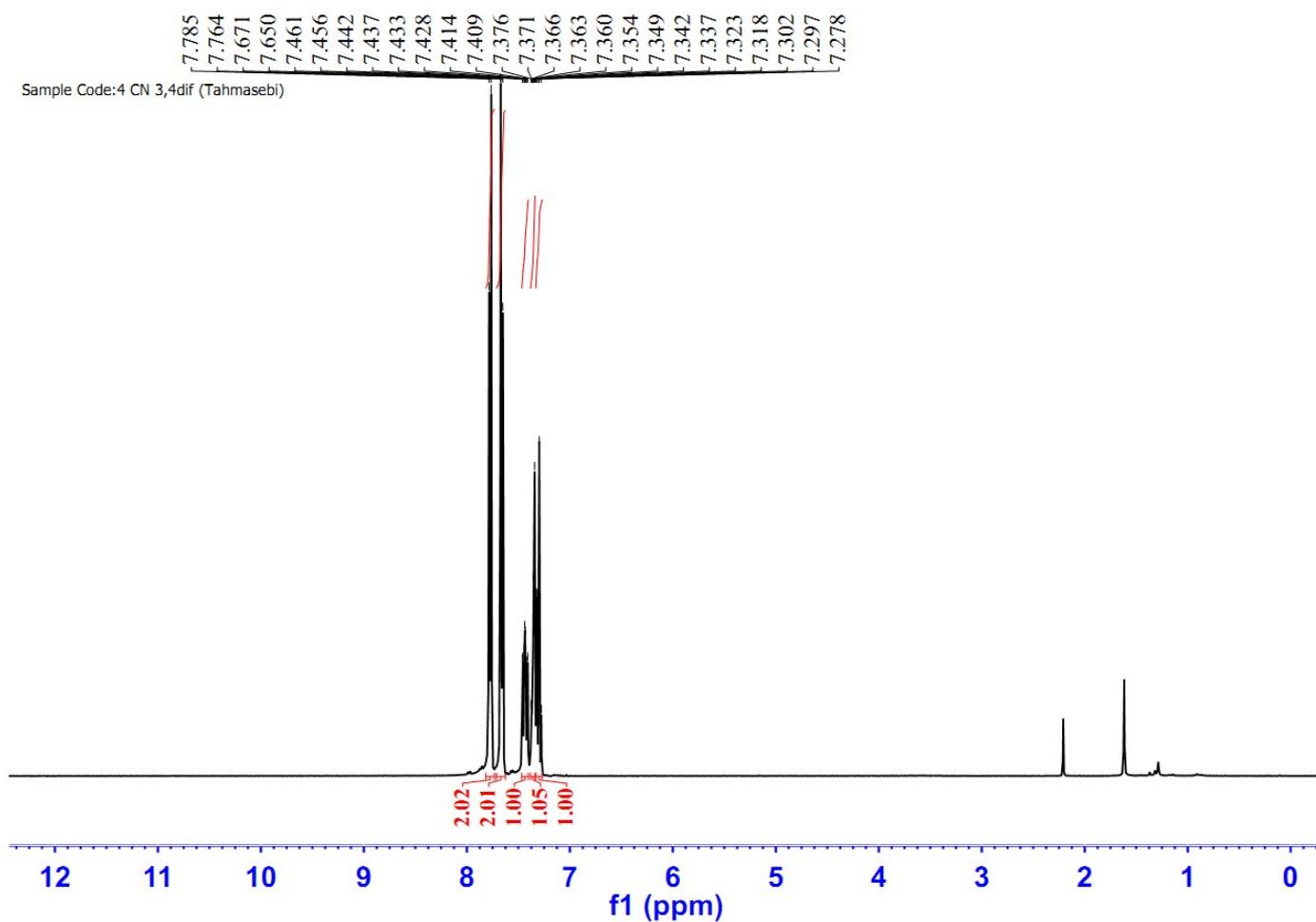


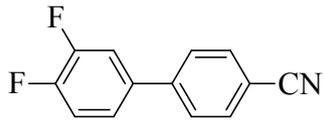
3,4-Difluoro-3'-methoxy-1,1'-biphenyl: ^{19}F NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = -137.7$ (d, 1F), -140.2 (d, 1F) ppm.



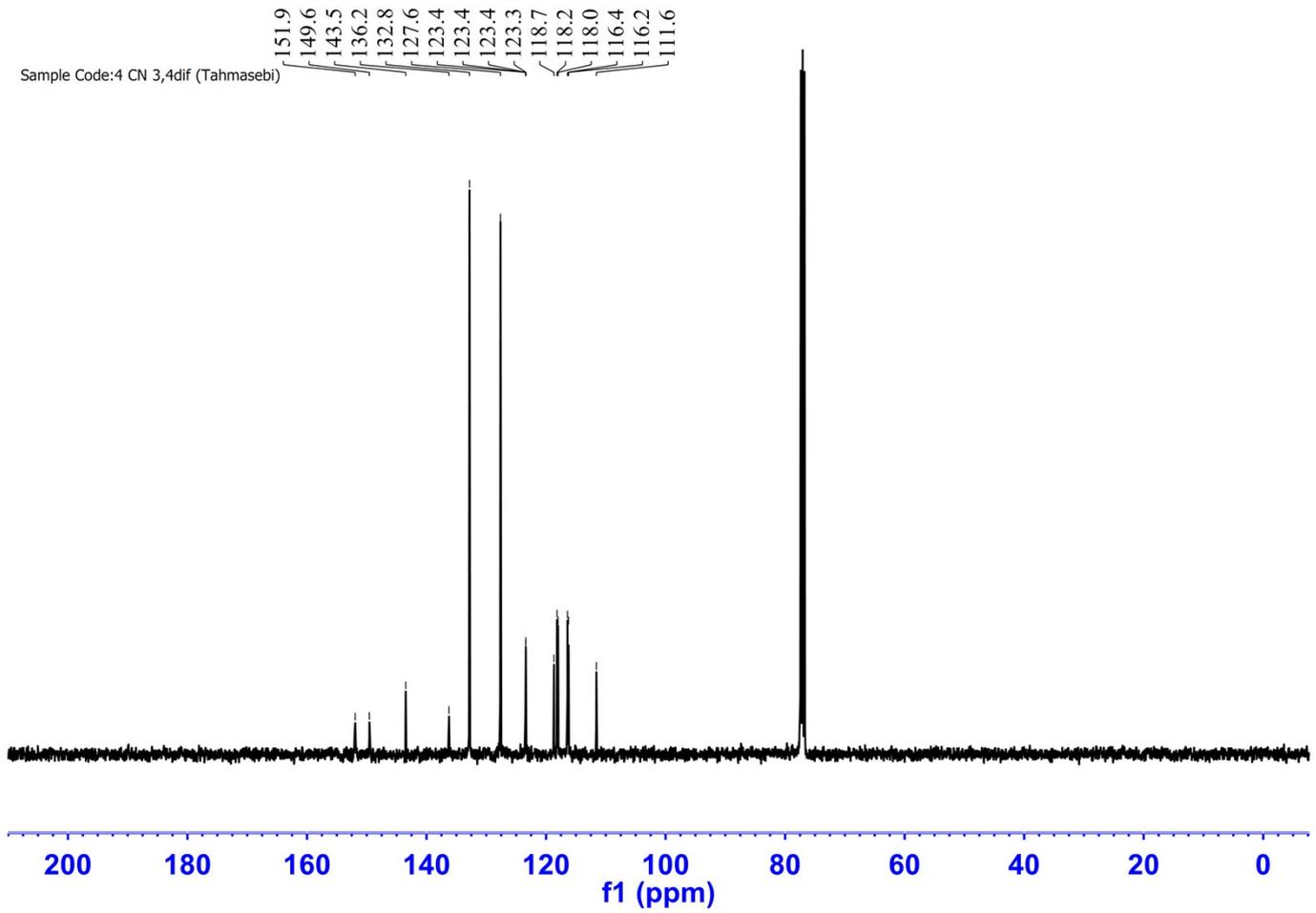


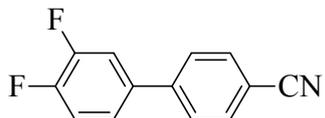
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.78\text{--}7.76$ (d, $J = 8\text{ Hz}$, 2H), $7.67\text{--}7.65$ (d, $J = 8\text{ Hz}$, 2H), $7.46\text{--}7.41$ (m, 1H), $7.38\text{--}7.34$ (m, 1H), $7.32\text{--}7.28$ (m, 1H) ppm.



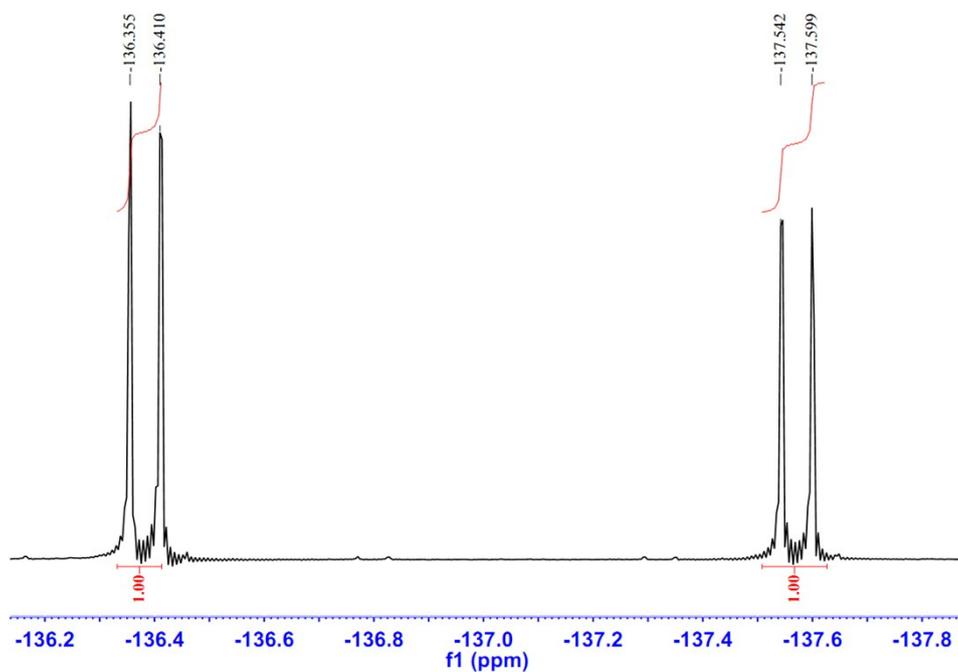
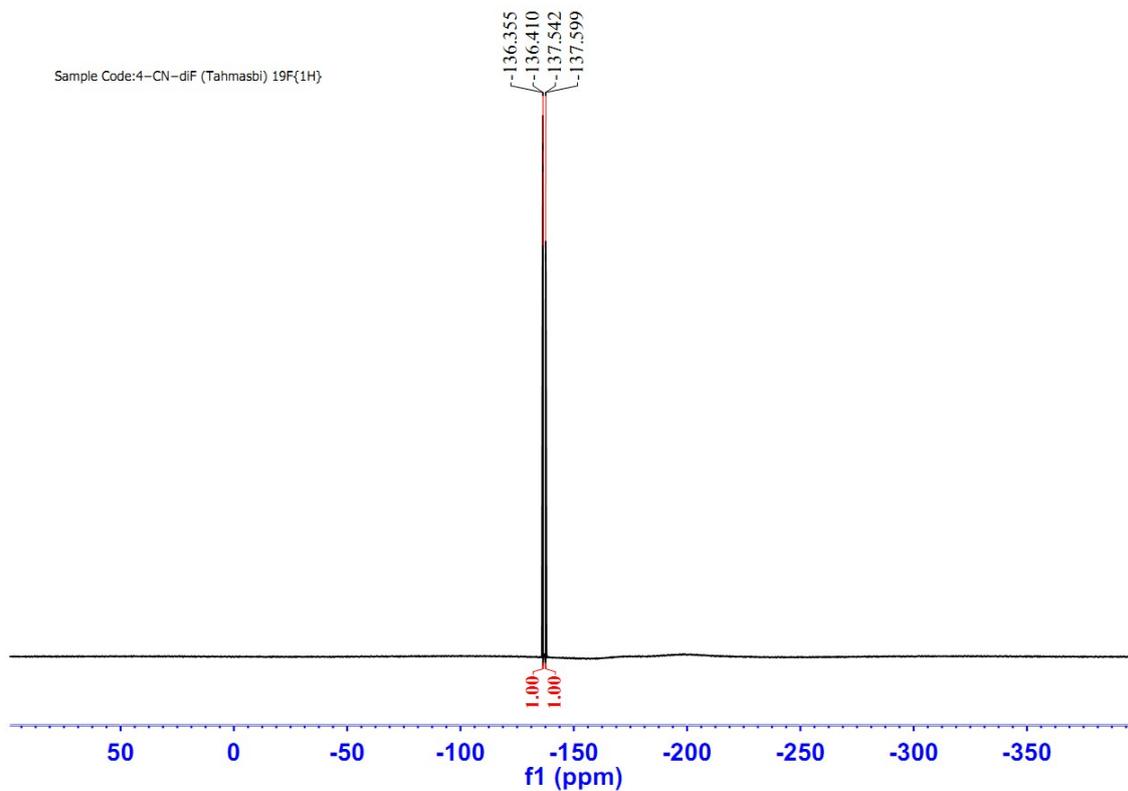


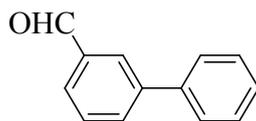
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: ^{13}C NMR (100 MHz, CDCl_3): $\delta = 151.9, 149.6, 143.5, 136.2, 132.8, 127.6, 123.4, 123.4, 123.4, 123.4, 123.3, 118.7, 118.2, 118.0, 116.4, 116.2, 111.6$ ppm.



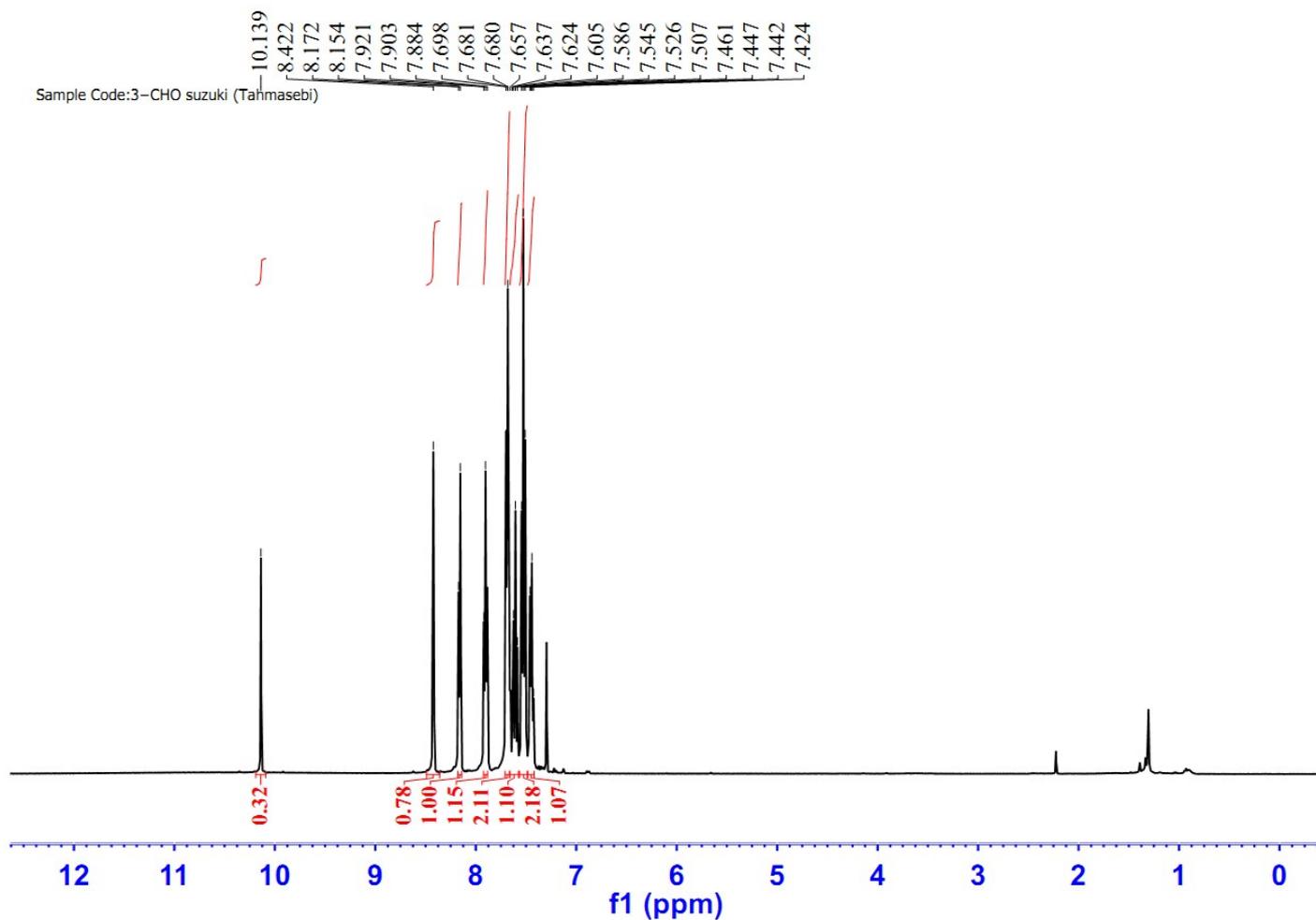


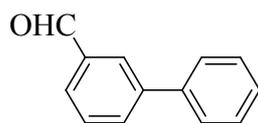
3',4'-Difluoro-[1,1'-biphenyl]-4-carbonitrile: ^{19}F NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = -136.4$ (d, 1F), -137.6 (d, 1F)ppm.



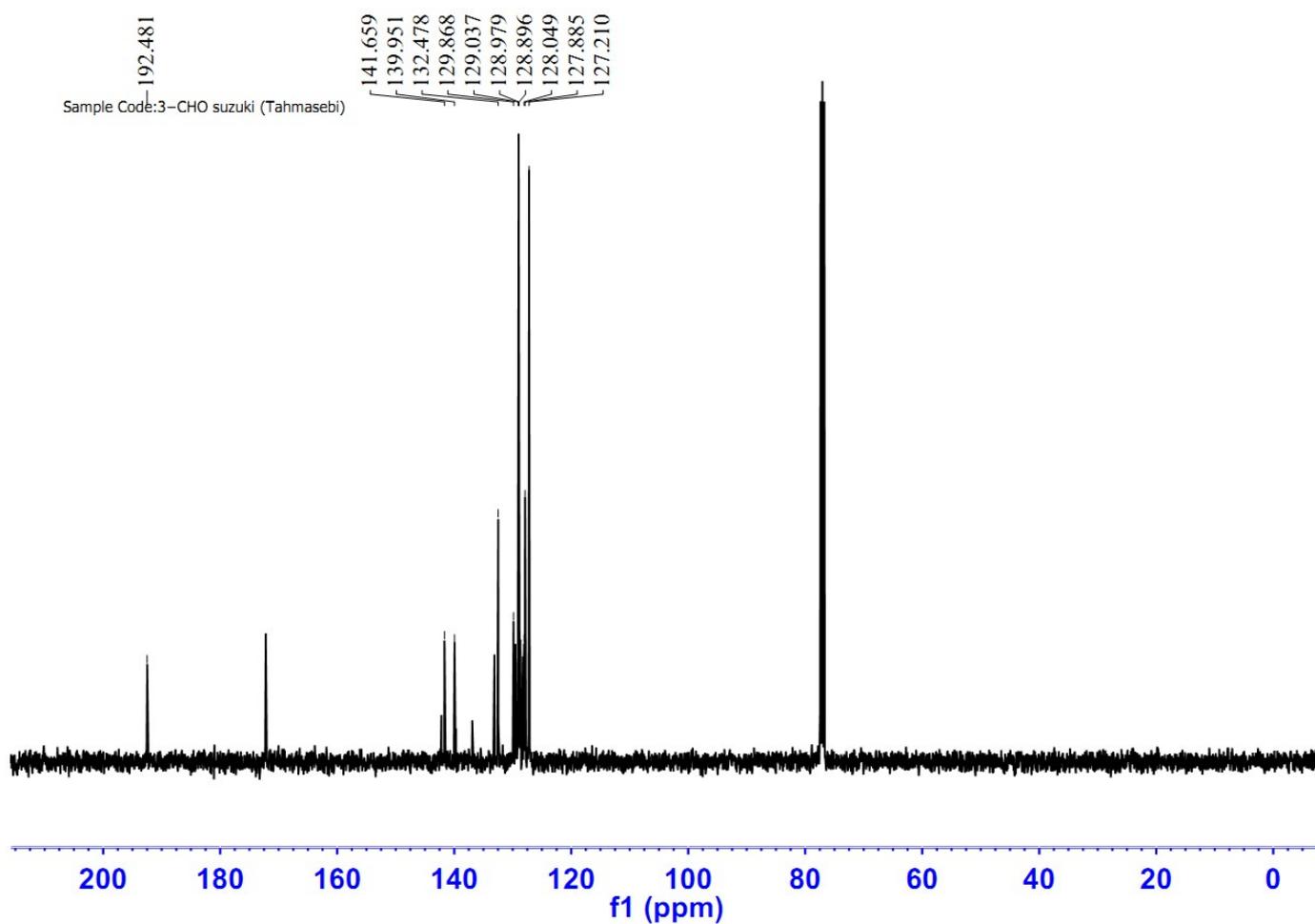


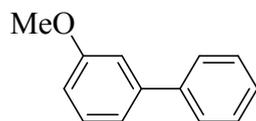
[1,1'-Biphenyl]-3-carbaldehyde: ^1H NMR (400 MHz, CDCl_3): δ_{H} = 10.14 (s, 1H), 8.42 (s, 1H), 8.17-8.15 (d, J = 8Hz, 1H), 7.9-7.88 (t, J = 8Hz, 1H), 7.70-7.66 (m, 2H), 7.63-7.58 (q, J = 8 Hz, 1H), 7.54-7.50 (t, J = 8 Hz, 2H), 7.46-7.42 (m, 1H) ppm.



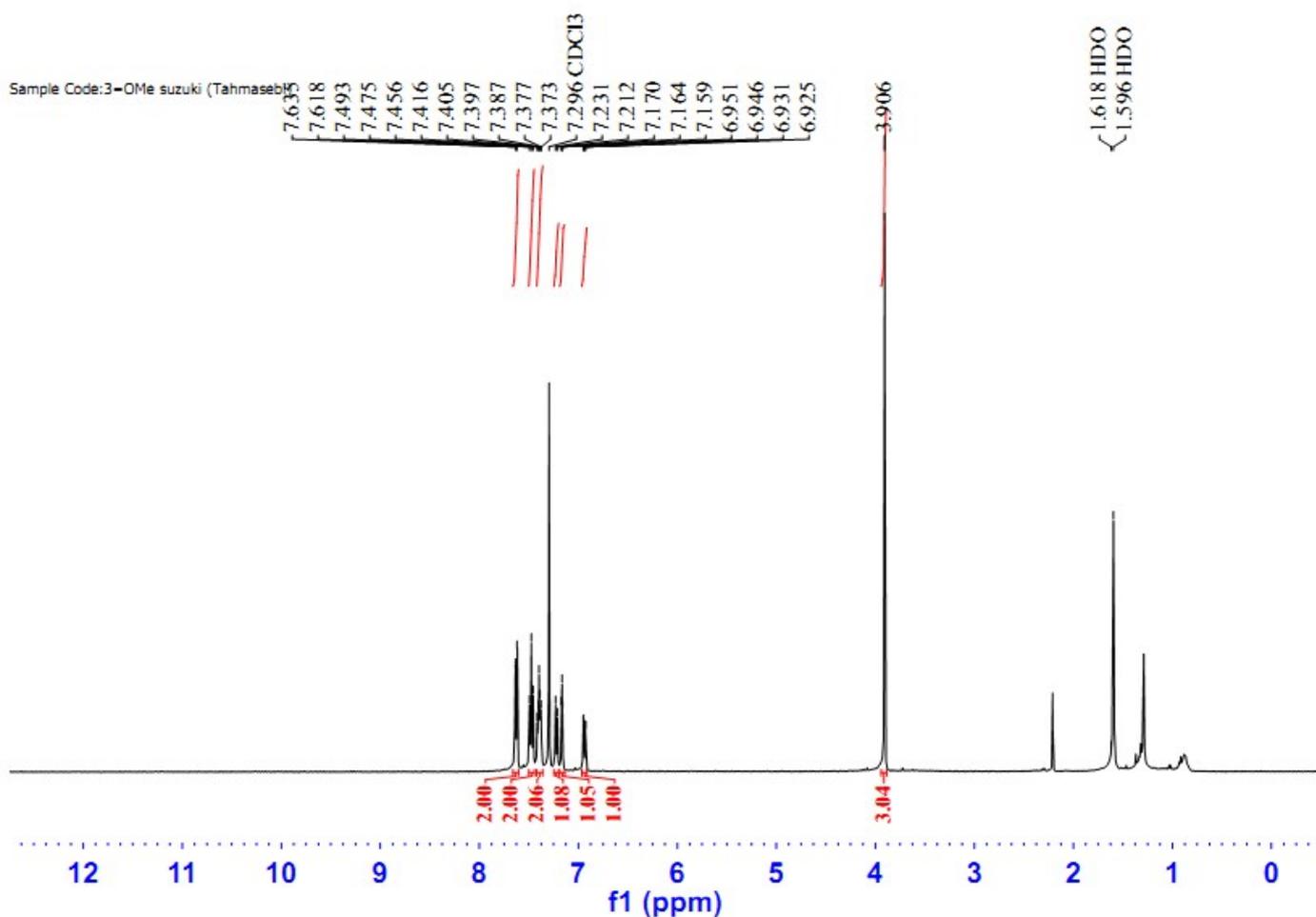


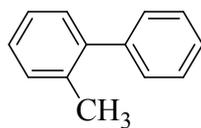
[1,1'-Biphenyl]-3-carbaldehyde: ^{13}C NMR (100 MHz, CDCl_3): $\delta = 192.5, 141.6, 139.9, 132.5, 129.9, 129.0, 129.0, 128.9, 128.0, 127.9, 127.2$ ppm.



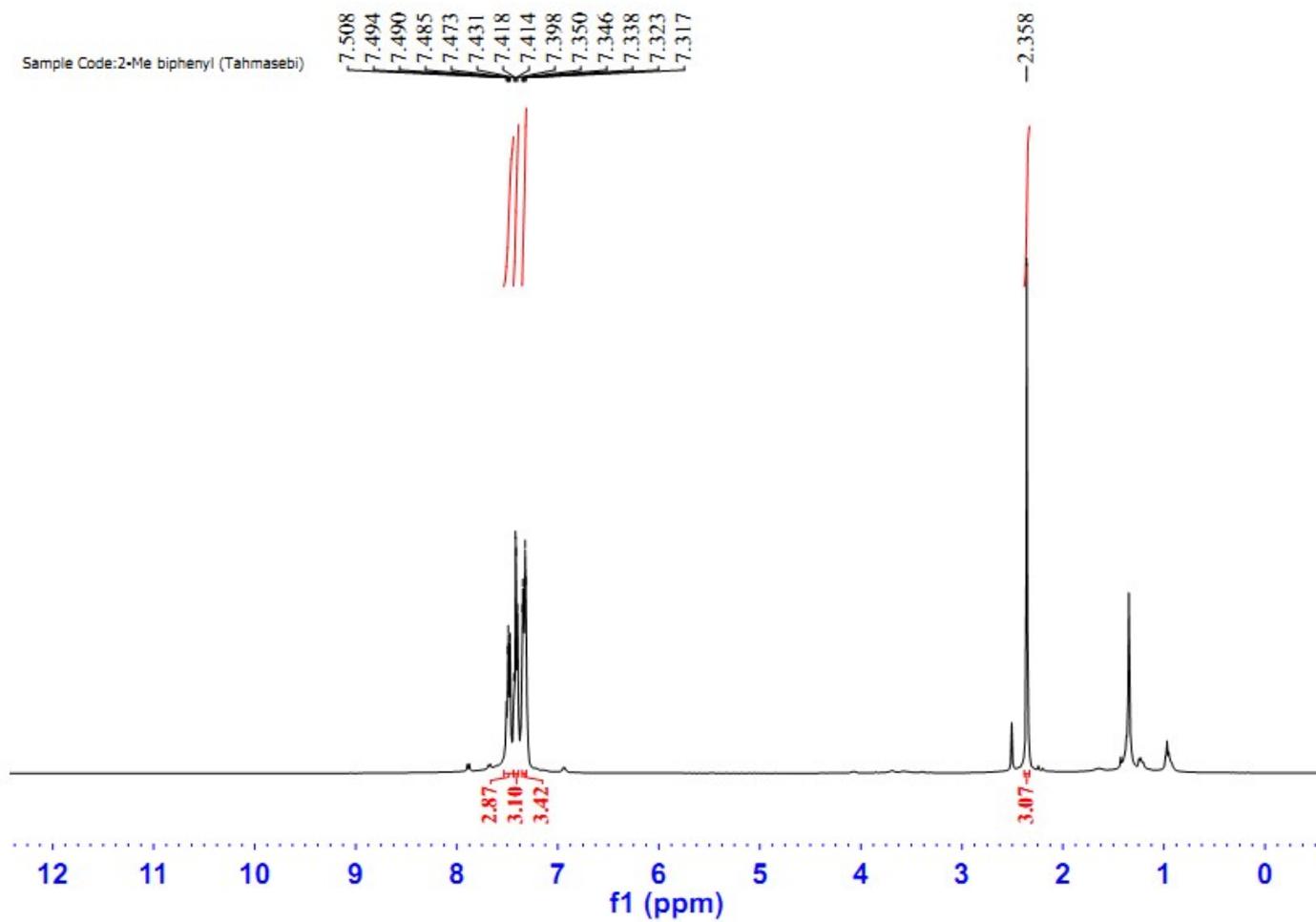


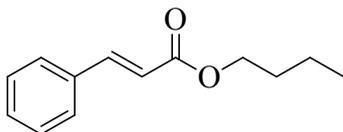
3-Methoxy-1,1'-biphenyl: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.64\text{--}7.62$ (d, $J = 8\text{ Hz}$, 2H), $7.49\text{--}7.45$ (t, $J = 8\text{ Hz}$, 2H), $7.42\text{--}7.37$ (six, $J = 4\text{ Hz}$, 2H), $7.23\text{--}7.21$ (d, $J = 8\text{ Hz}$, 1H), $7.17\text{--}7.15$ (t, $J = 4\text{ Hz}$, 1H), $6.95\text{--}6.92$ (dd, $J = 8\text{ Hz}$, $J = 4\text{ Hz}$, 1H), 3.91 (s, 3H) ppm.



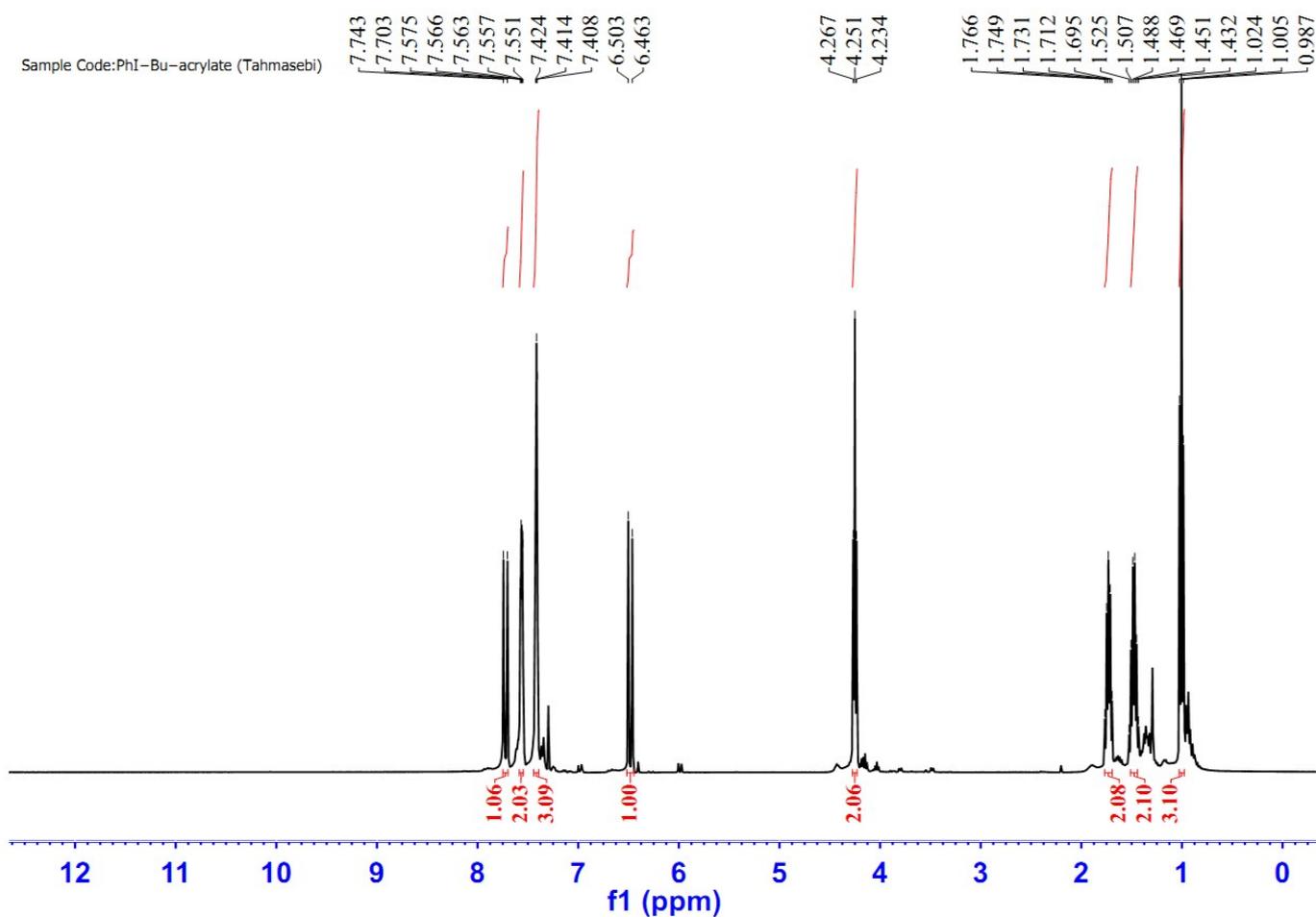


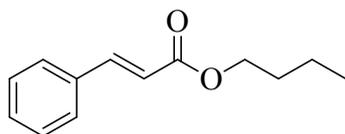
2-Methyl-1,1'-biphenyl: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.51\text{-}7.47$ (t, $J = 8\text{ Hz}$, 3H), $7.44\text{-}7.40$ (t, $J = 8\text{ Hz}$, 3H), $7.35\text{-}7.32$ (m, 3H), 2.36 (s, 3H) ppm.



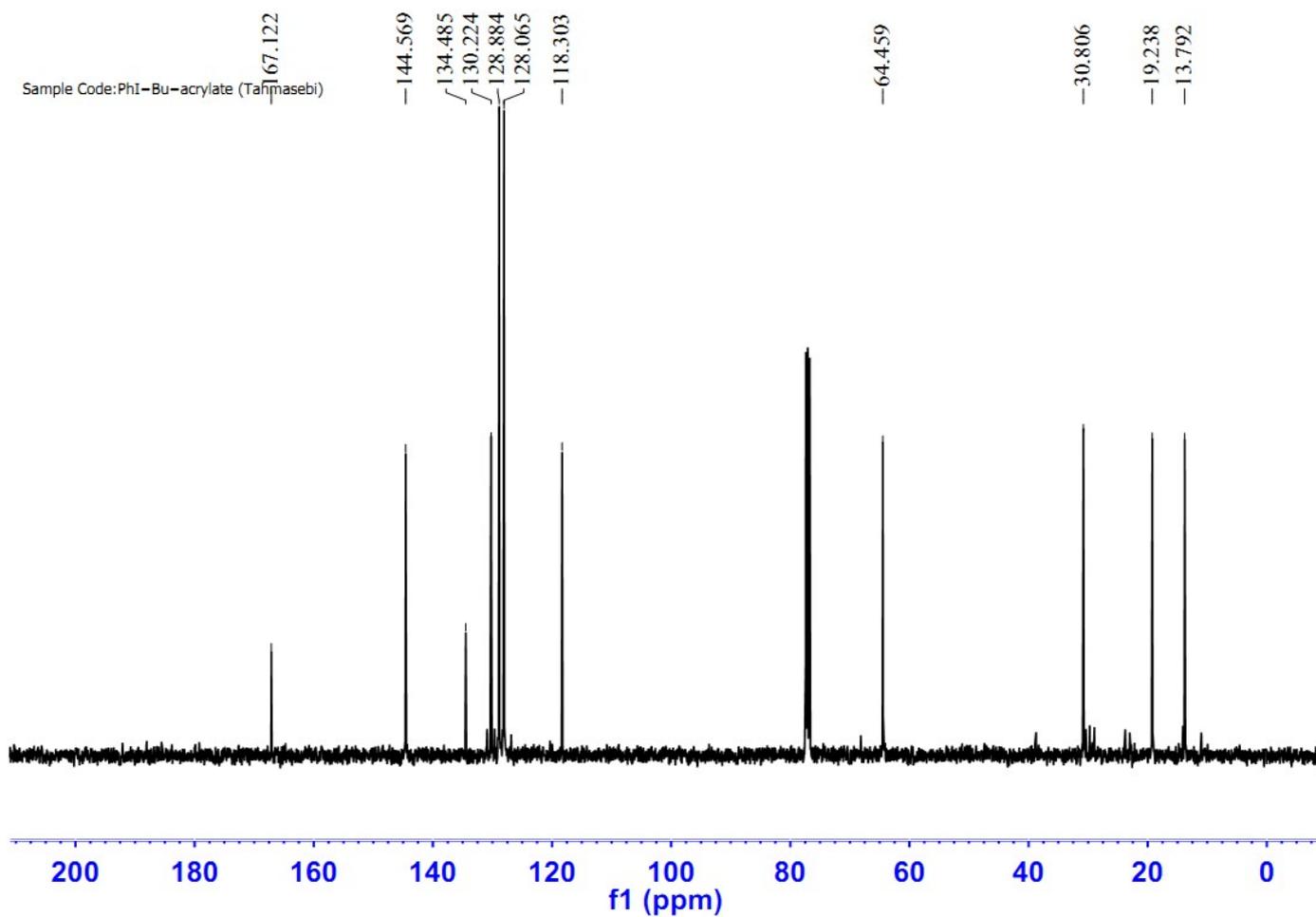


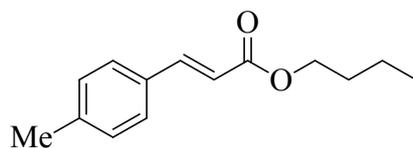
Butyl cinnamate: ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.74-7.70 (d, J = 16 Hz, 1H), 7.57-7.55 (m, 2H), 7.42-7.40 (t, J = 4 Hz, 3H), 6.50-6.46 (d, J = 16 Hz, 1H), 4.27-4.23 (t, J = 8 Hz, 2H), 1.77-1.69 (quint, J = 8 Hz, 2H), 1.52-1.43 (sextet, J = 8 Hz, 2H), 1.02-0.98 (t, J = 8 Hz, 3H) ppm.



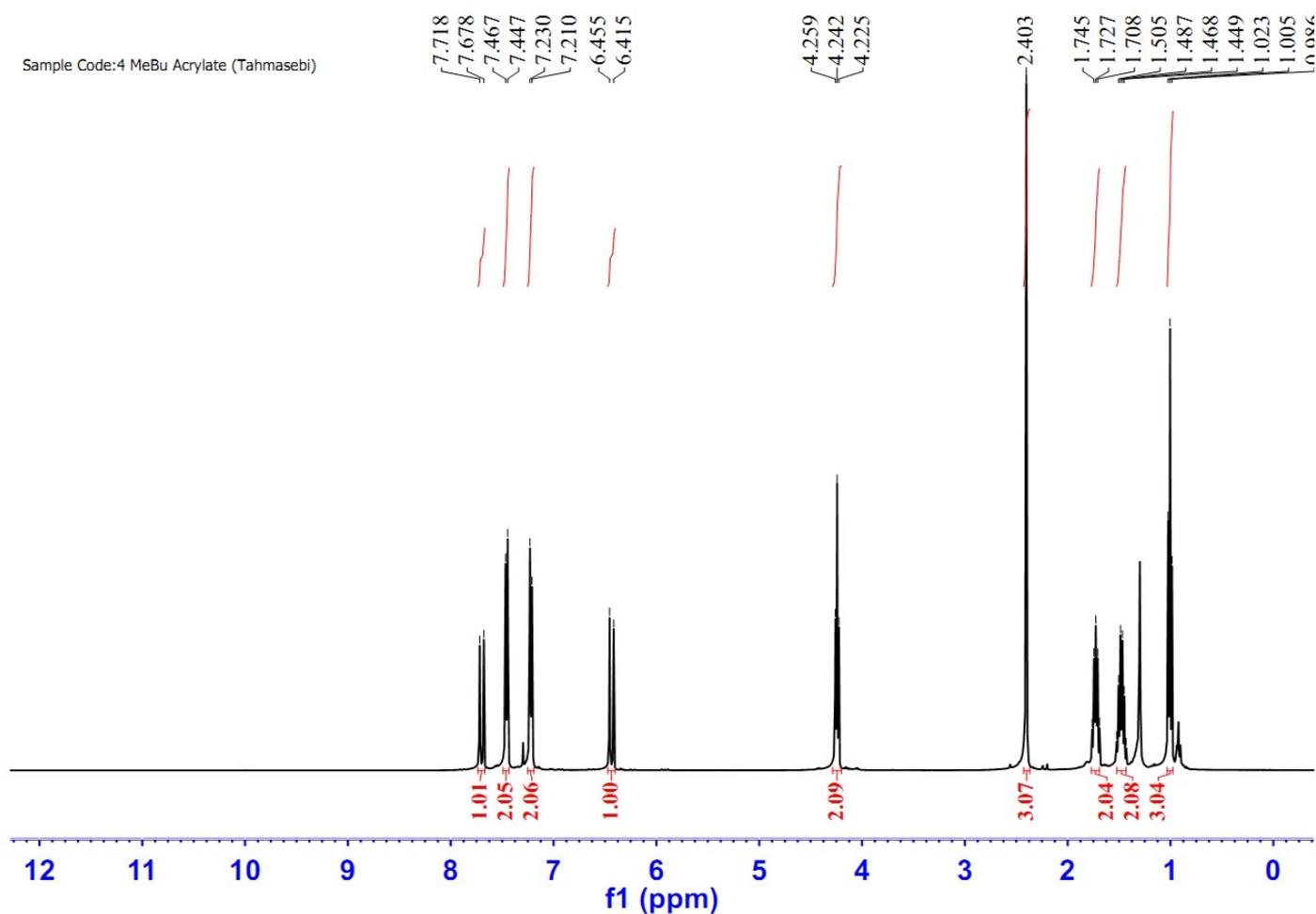


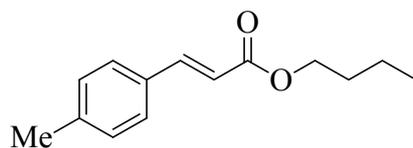
Butyl cinnamate: ^{13}C NMR (100 MHz, CDCl_3): $\delta=167.1, 144.6, 134.5, 130.2, 128.9, 128.1, 118.3, 64.4, 30.8, 19.2, 13.8$ ppm.



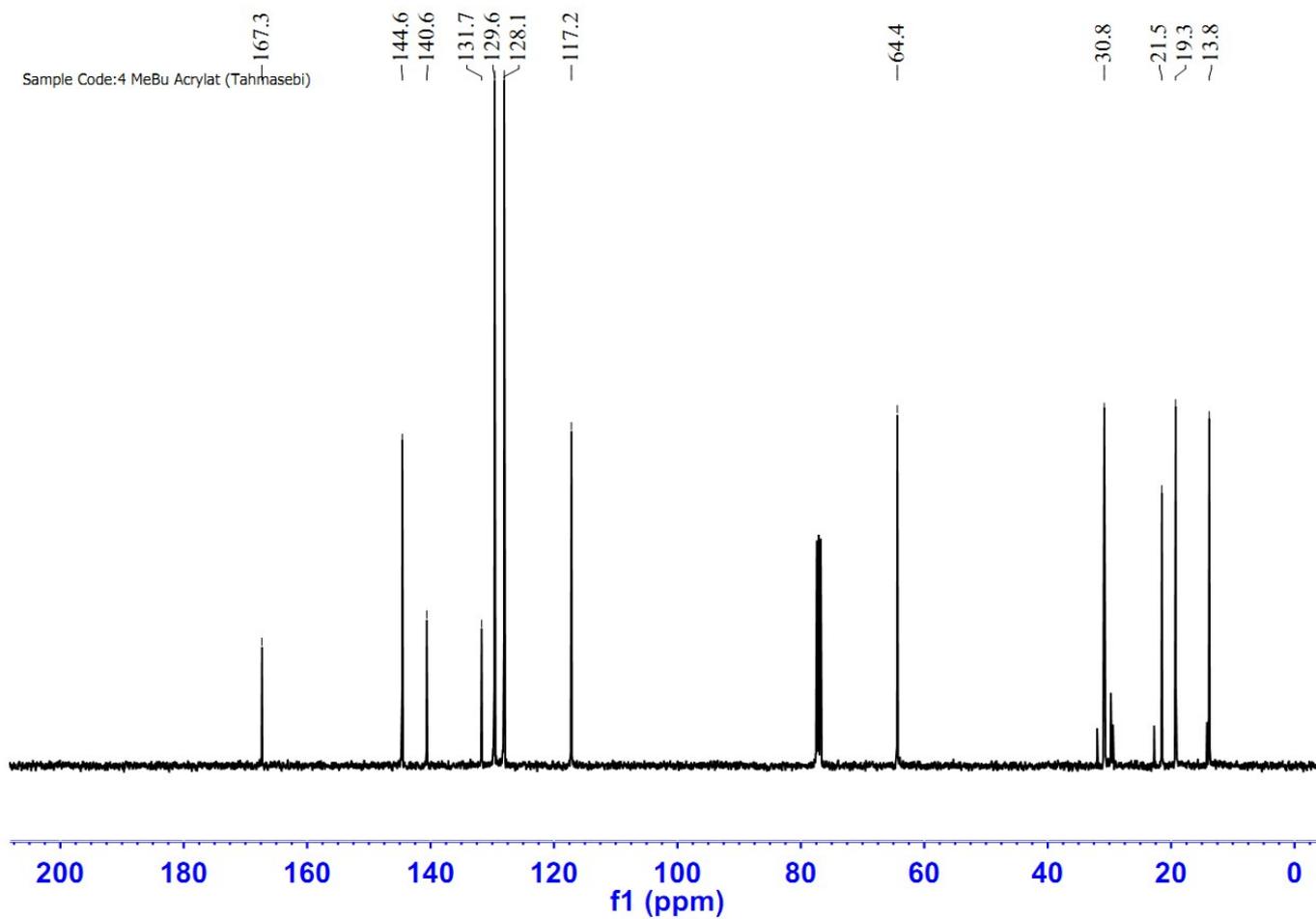


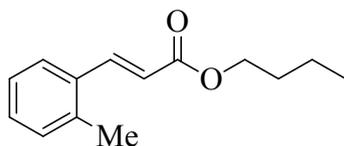
Butyl 3-(4-methylphenyl)acrylate: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.72\text{--}7.68$ (d, $J = 16$ Hz, 1H), $7.48\text{--}7.45$ (d, $J = 12$ Hz, 2H), $7.23\text{--}7.21$ (d, $J = 8$ Hz, 2H), $6.45\text{--}6.41$ (d, $J = 16$ Hz, 1H), $4.26\text{--}4.22$ (t, $J = 8$ Hz, 2H), 2.40 (s, 3H), $1.76\text{--}1.69$ (quint, $J = 8$ Hz, 2H), $1.52\text{--}1.43$ (sextet, $J = 8$ Hz, 2H), $1.02\text{--}0.98$ (t, $J = 8$ Hz, 3H) ppm.



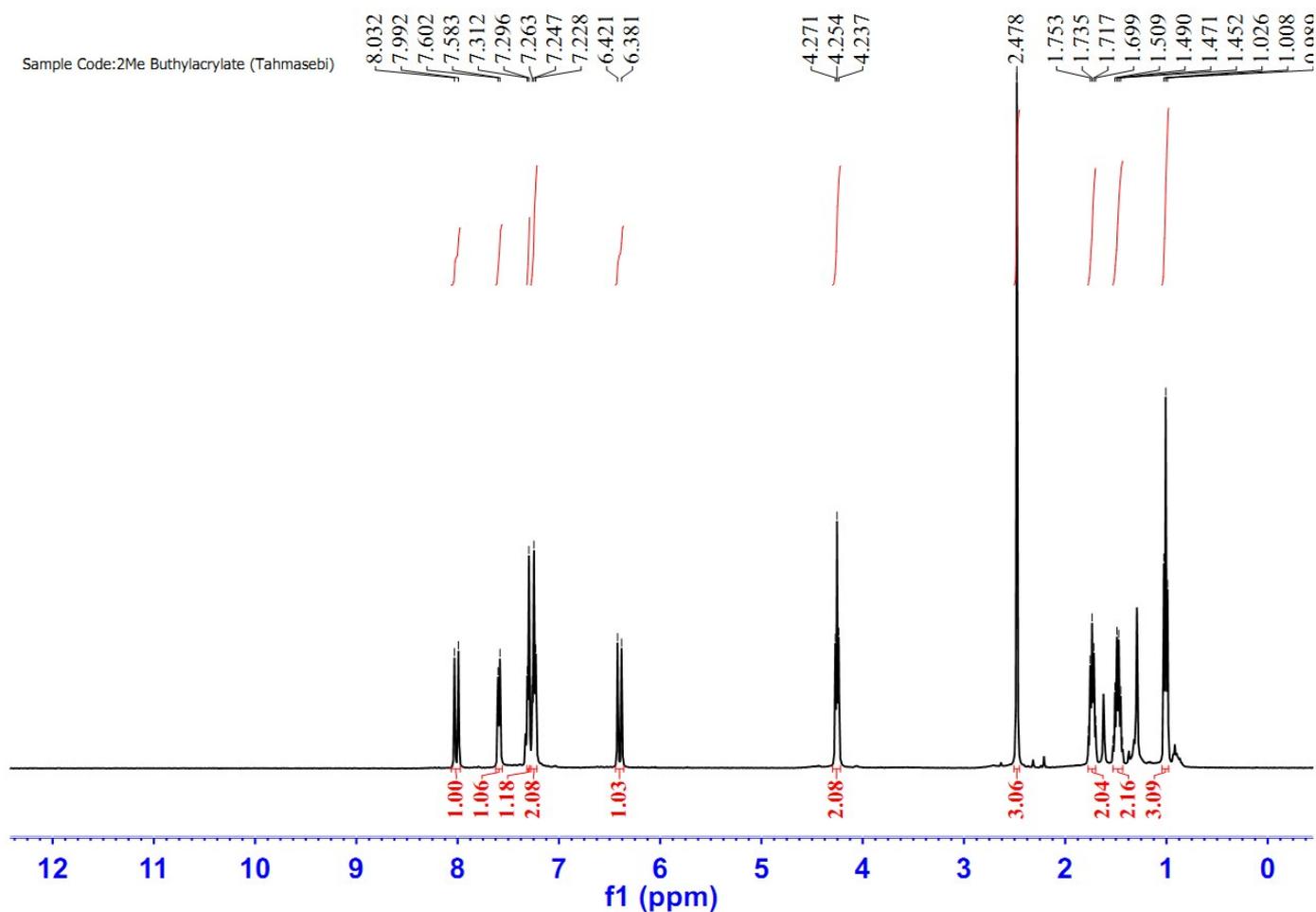


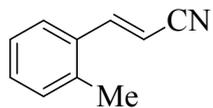
Butyl 3-(4-methylphenyl)acrylate: ^{13}C NMR (100 MHz, CDCl_3): $\delta=167.3, 144.6, 140.6, 131.7, 129.6, 128.1, 117.2, 64.4, 30.8, 21.5, 19.3, 13.8$ ppm.



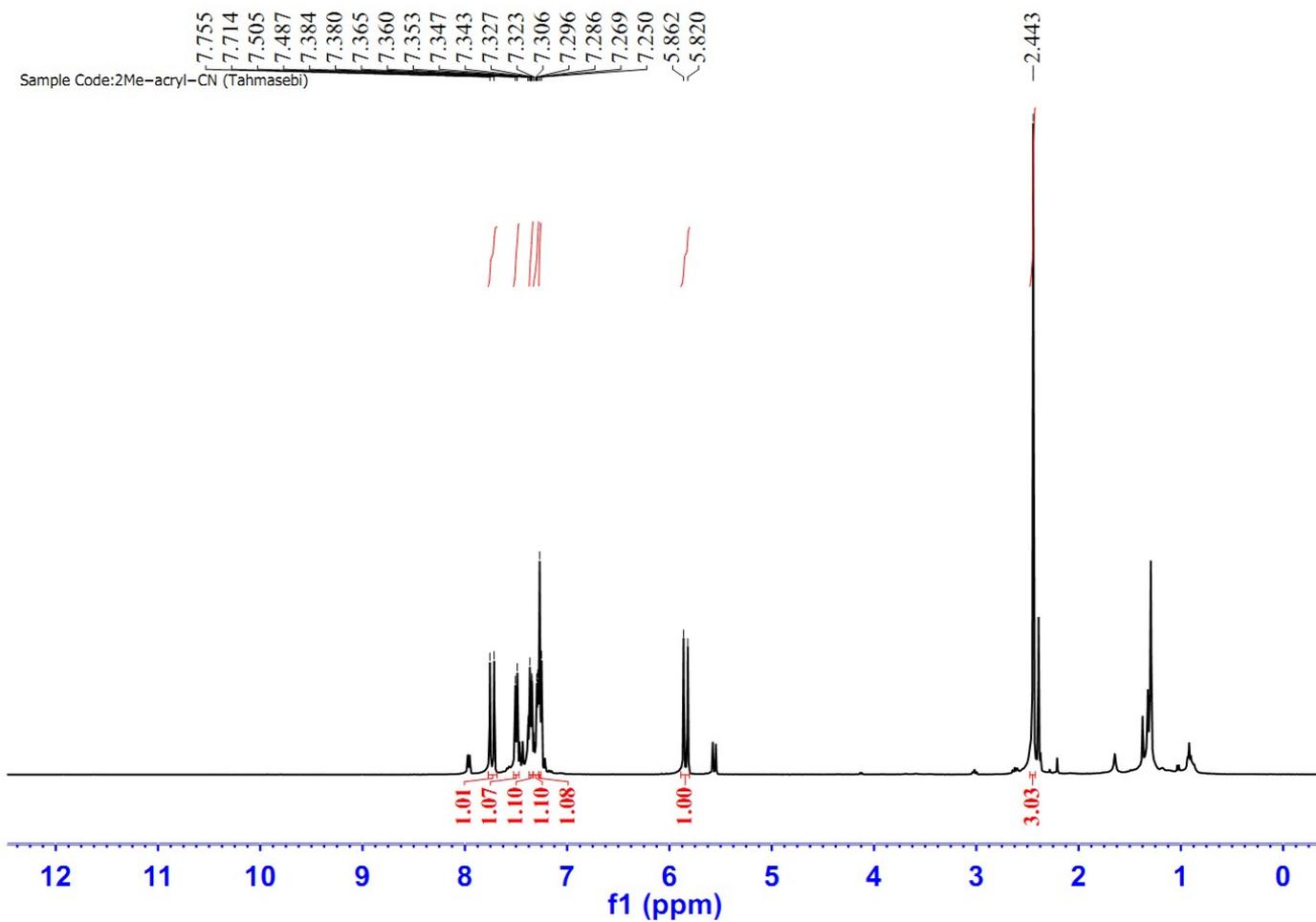


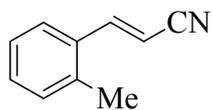
Butyl 3-(2-methylphenyl)acrylate: ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.803-7.992 (d, J = 16 Hz, 1H), 7.60-7.58 (d, J = 8 Hz, 1H), 7.31-7.30 (d, J = 4 Hz, 1H), 7.26-7.2 (t, J = 8 Hz, 2H), 6.42-6.38 (d, J = 16 Hz, 1H), 4.27-4.23 (t, J = 8 Hz, 2H), 2.48 (s, 3H), 1.77-1.70 (quint, J = 8 Hz, 2H), 1.53-1.43 (sextet, J = 8 Hz, 2H), 1.02-0.98 (t, J = 8 Hz, 3H) ppm.



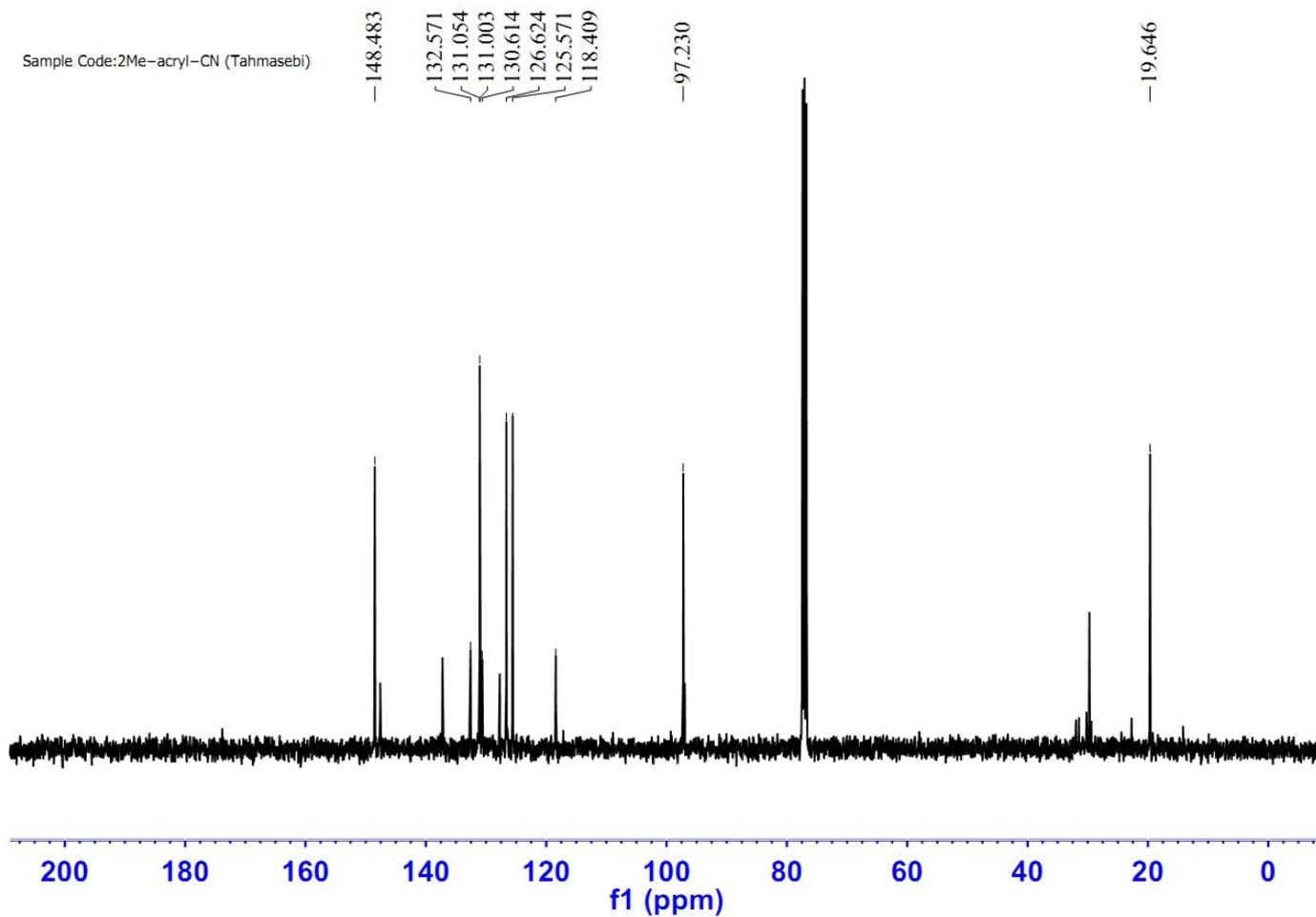


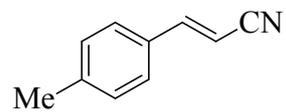
3-(*o*-Tolyl)acrylonitrile: ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.75-7.71 (d, J = 16 Hz, 1H), 7.50-7.49 (d, J = 4 Hz, 1H), 7.38-7.34 (d, J = 8 Hz, 1H), 7.33-7.29 (m, 1H), 7.27-7.25 (d, J = 8 Hz, 1H), 5.86-5.82 (d, J = 16 Hz, 1H), 2.44 (s, 3H) ppm.



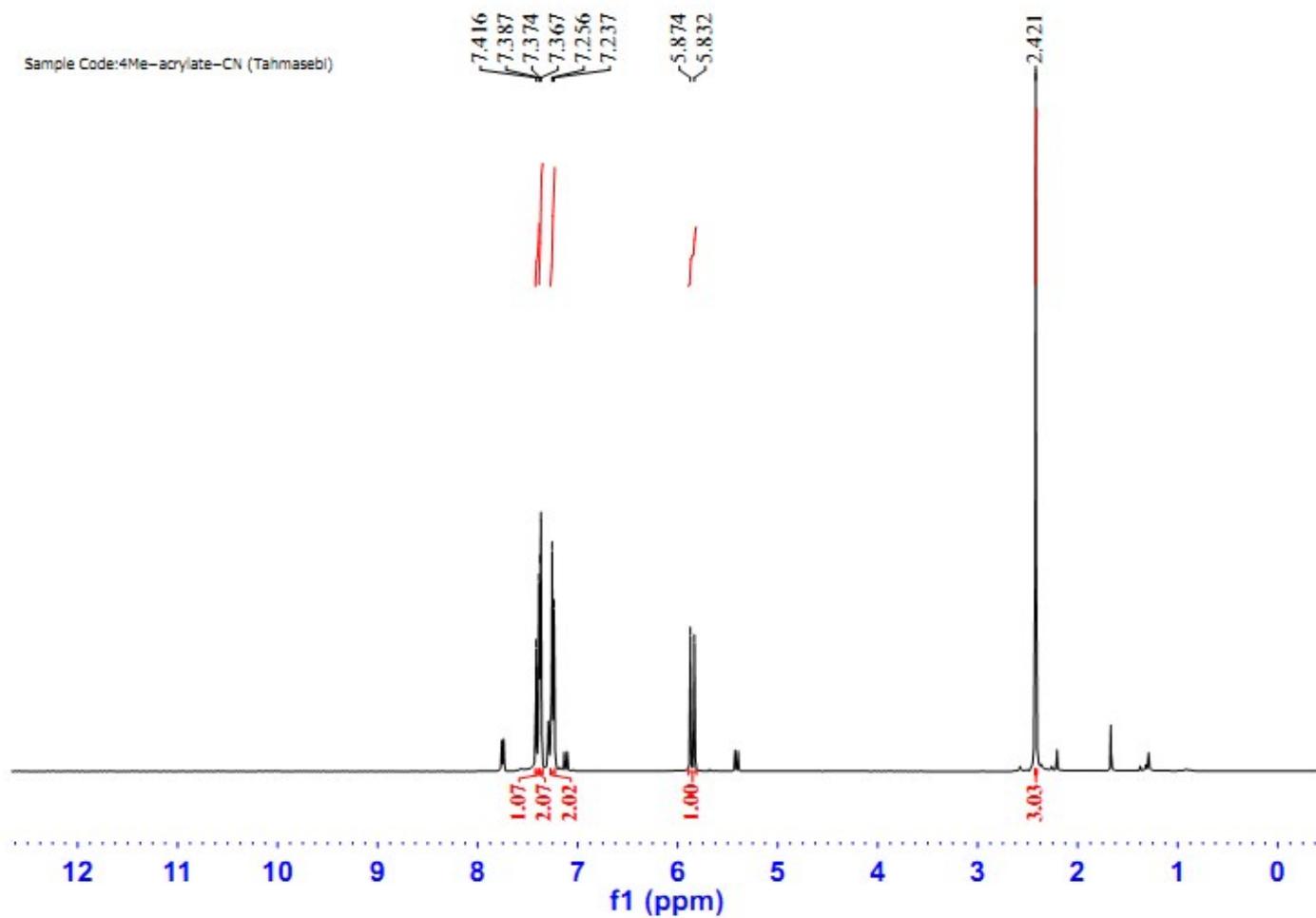


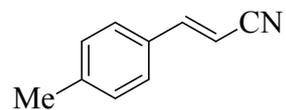
3-(o-Tolyl)acrylonitrile: ^{13}C NMR (100 MHz, CDCl_3): $\delta=148.5, 132.6, 131.1, 131.0, 130.6, 126.6, 125.6, 118.4, 97.2, 19.6$ ppm.



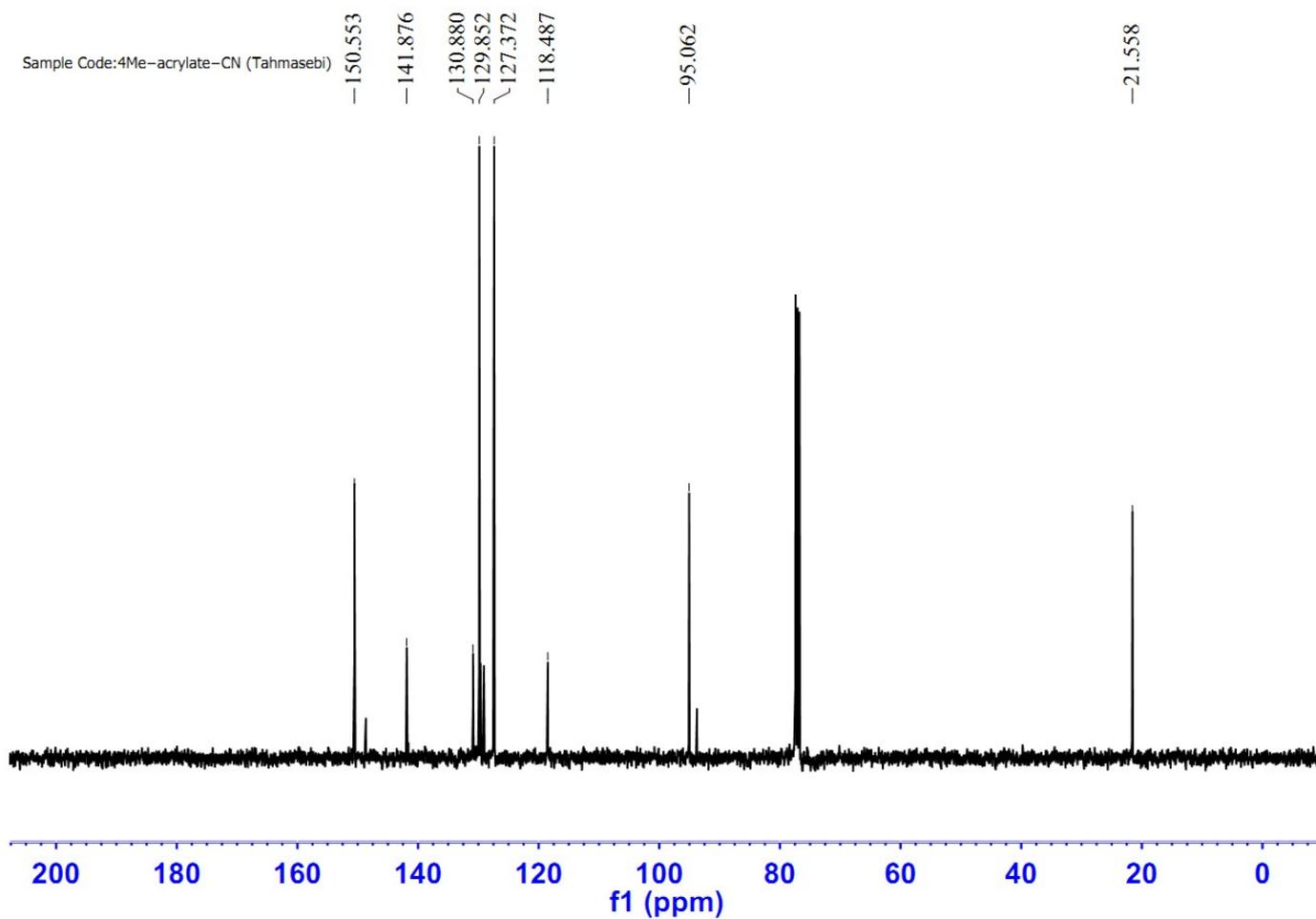


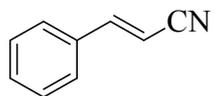
3-(p-Tolyl)acrylonitrile: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.42\text{-}7.38$ (d, $J = 16$ Hz, 1H), $7.37\text{-}7.36$ (d, $J = 4$ Hz, 2H), $7.26\text{-}7.24$ (d, $J = 8$ Hz, 2H), $5.87\text{-}5.83$ (d, $J = 16$ Hz, 1H), 2.42 (s, 3H) ppm.



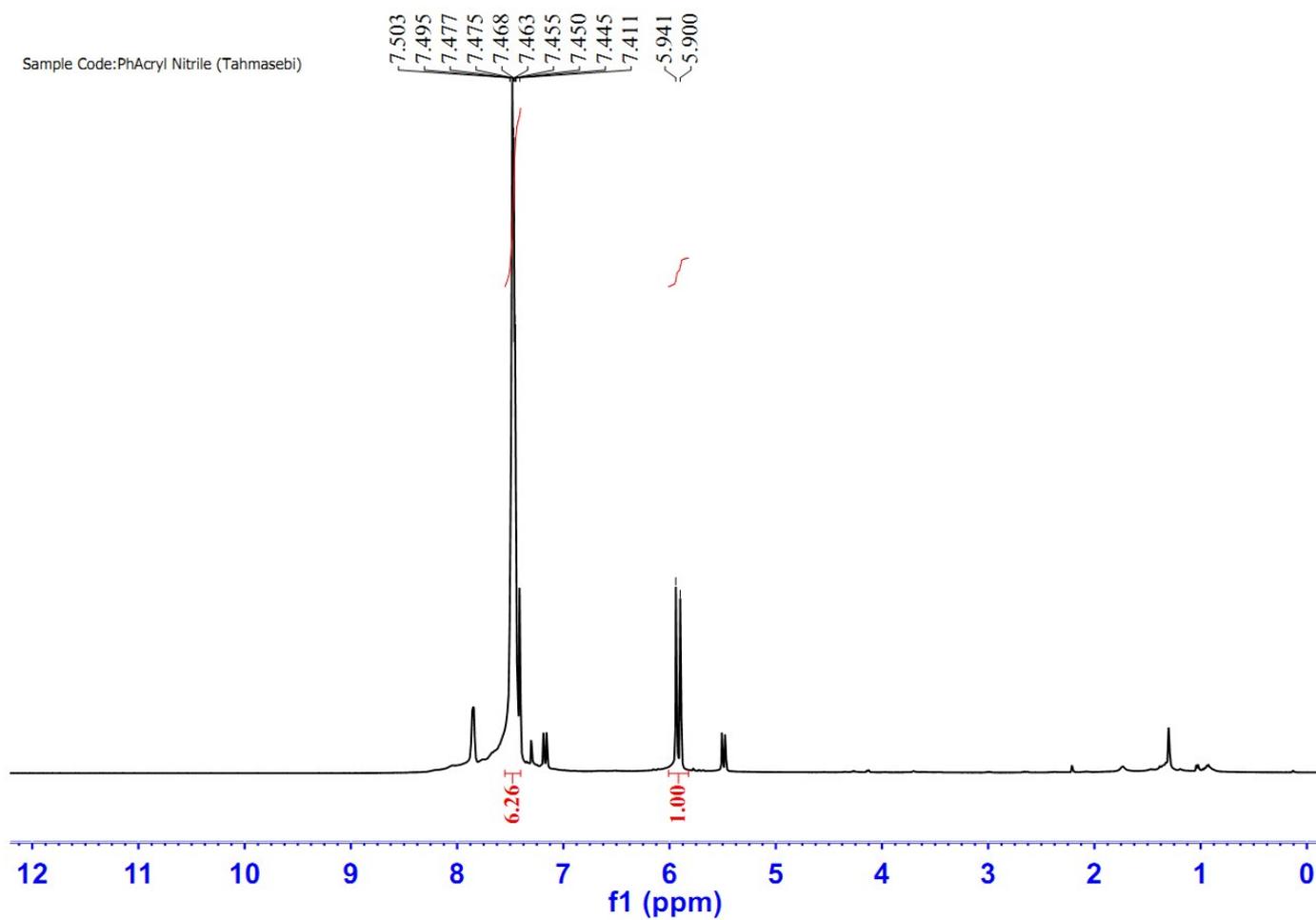


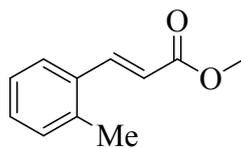
3-(p-Tolyl)acrylonitrile: ^{13}C NMR (100 MHz, CDCl_3): $\delta=150.5, 141.9, 130.9, 129.8, 127.4, 118.5, 95.1, 21.5$ ppm.



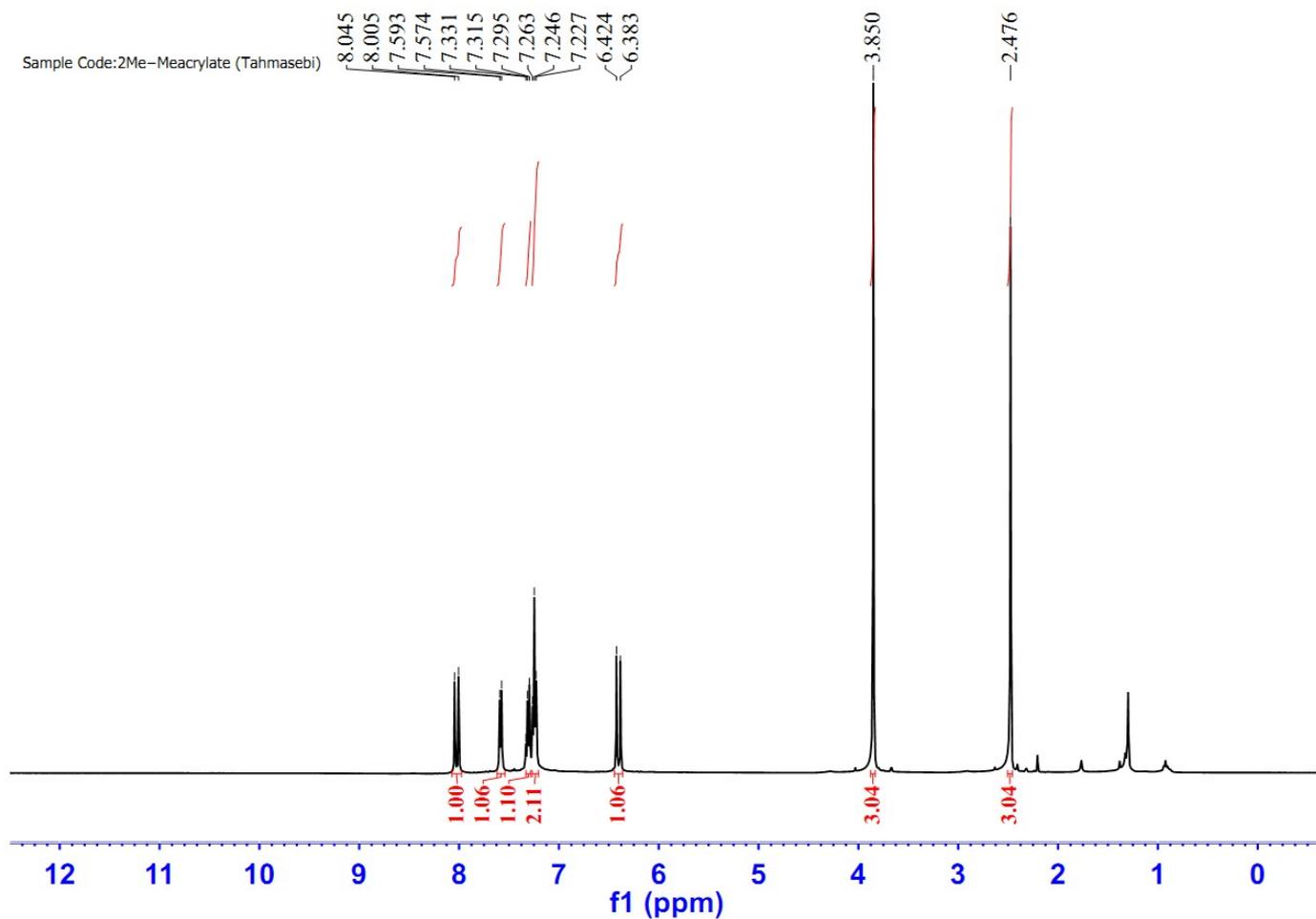


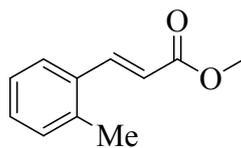
Cinnamitrile: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 7.53\text{--}7.41$ (m, 6H), 5.94–5.90 (d, $J = 16$ Hz, 1H) ppm.



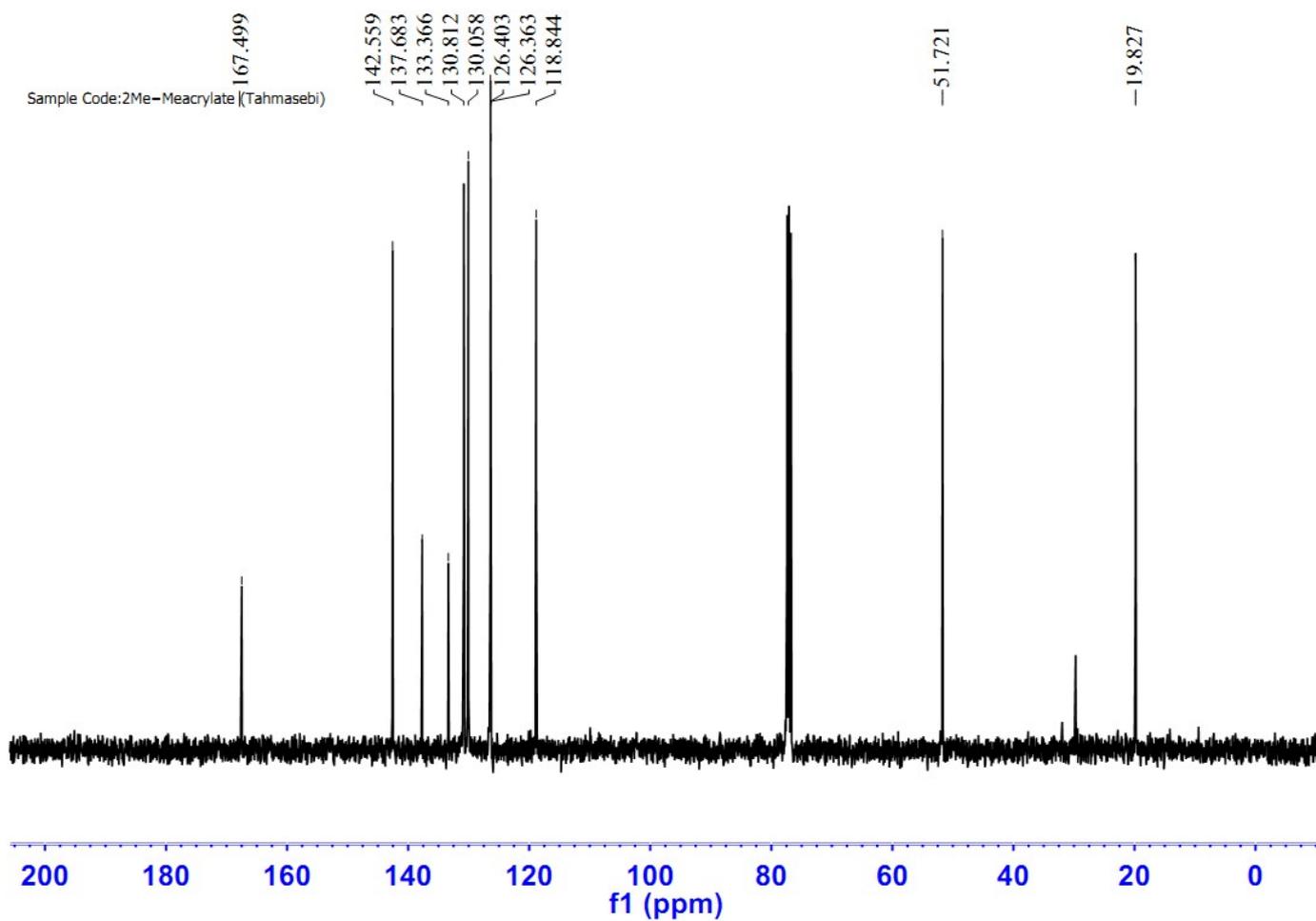


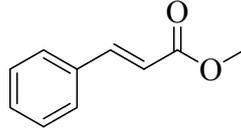
Methyl 3-(*o*-tolyl)acrylate: ^1H NMR (400 MHz, CDCl_3): $\delta_{\text{H}} = 8.04\text{--}8.00$ (d, $J = 16$ Hz, 1H), $7.59\text{--}7.57$ (d, $J = 8$ Hz, 1H), $7.33\text{--}7.29$ (t, $J = 8$ Hz, 1H), $7.26\text{--}7.23$ (t, $J = 8$ Hz, 2H), $6.42\text{--}6.38$ (d, $J = 16$ Hz, 1H), 3.85 (s, 3H), 2.48 (s, 3H) ppm.



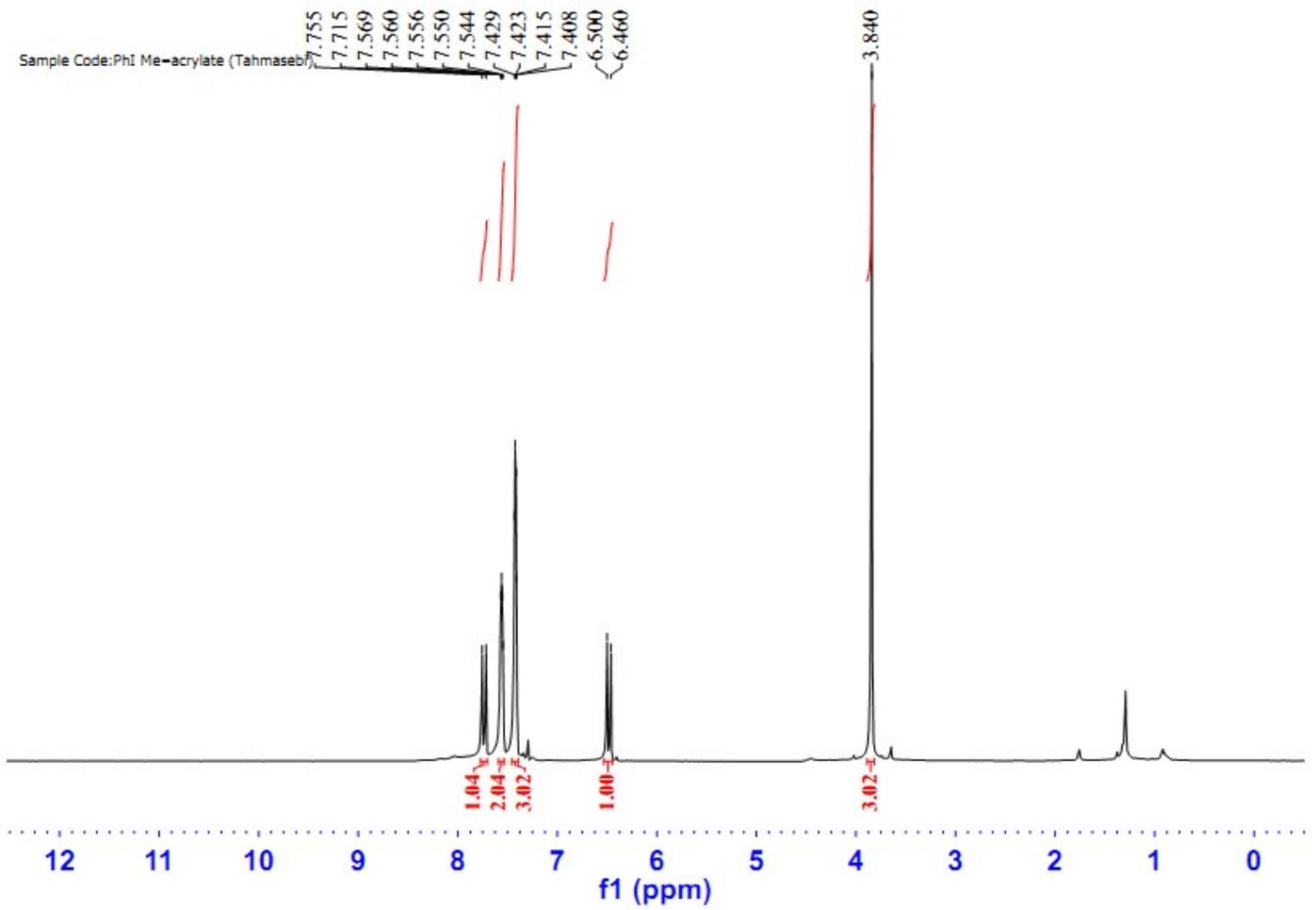


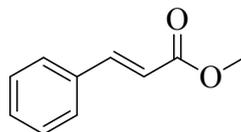
Methyl 3-(o-tolyl)acrylate: ^{13}C NMR (100 MHz, CDCl_3): $\delta=167.5, 142.5, 137.7, 133.4, 130.8, 130.0, 126.4, 126.3, 118.8, 51.7, 19.8$ ppm.





Methyl cinnamate: ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.75-7.71 (d, J = 16 Hz, 1H), 7.57-7.54 (m, 2H), 7.43-7.41 (m, 3H), 6.50-6.46 (d, J = 16 Hz, 1H), 3.84 (s, 3H) ppm.





Methyl cinnamate: ^{13}C NMR (100 MHz, CDCl_3): $\delta=167.4, 144.9, 134.4, 130.3, 128.9, 128.1, 117.8, 51.7$ ppm.

